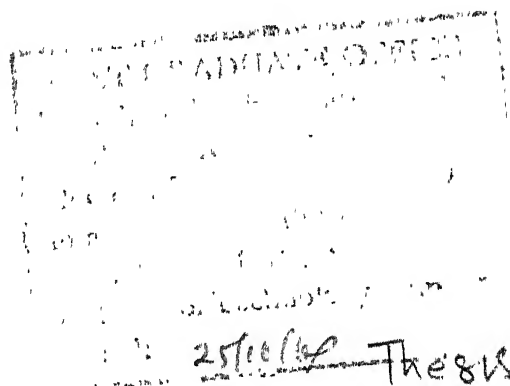


Nuclear Magnetic Relaxation in Coupled Spin Systems by Double Resonance

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There the snow lay great heaps
of protons quietly precessing in the
earth's magnetic field.

— E.M. Purcell

Nobel Lecture 1952

Certified that the work described in this thesis
is the original work of Mr. Anil Kumar done under my
supervision.

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SYNOPSIS

This thesis presents a study of nuclear magnetic relaxation in coupled spin systems in liquids, by steady-state homonuclear double resonance. The n.m.r. spectra of most liquids under high resolution show a multiplet structure. These spectra normally exhibit little information on spin relaxation processes operative in the system. The relaxation in these systems can be studied by double resonance experiments, in which one of the transitions in the spectrum is irradiated by a strong r.f. field while the remaining part of the spectrum is observed by a second weak r.f. field. Irradiation causes features in the spectrum which depend on relaxation. An analysis of these features leads to significant information about the mechanisms of relaxation. Double resonance experiments in this work, were performed on the coupled spin systems of (i) ring protons of 2,6-dibromoaniline (AB_2 spin system) and (ii) of 2-bromothiazole (AB spin system). These experiments were performed with a view to study the systematics of the method and details of the relaxation processes. The motivation of this study and a brief review of earlier work is given in the introductory chapter of the thesis.

The notation and the density-matrix method of analysis, used in this work, are presented in Chapter IIA. The inhomogeneity of the static magnetic field is found to play an important role in the interpretation of the relaxation effects and a method of including it in the density-matrix calculations and of determining its contribution to single and double resonance transitions is given in Sec. IIB. The distinctive features of solutions of density-matrix equations for low and high strengths of irradiation, which have been found to be useful in the analysis, are discussed in Sec. IIC, along with a graphical method for interpretation of the spectra with low strengths of irradiation.

Various mechanisms responsible for proton relaxation are described in Chapter III. It is often convenient to use ~~as~~ the model of an isotropic external random field for the description of relaxation effects. This model includes the overall effect of various interactions, explicit considerations of which are rather involved. The conditions under which various relaxation mechanisms can be approximated by a random field and the degree of correlation between these fields at the sites of different spins are discussed. It is shown that under conditions normally used in the experiments, several of the mechanisms can be approximated by a random field. Scalar coupling interaction is also examined and

the conditions under which it can be treated only as a mechanism for relaxation are discussed.

The frequency-sweep homonuclear double resonance experiments were performed by adding auxiliary apparatus, to the Varian HR-100 spectrometer with appropriate modifications. The details of the experimental set-up are given in Chapter IV.

In Chapter V, results of double resonance experiments performed on the ring proton (AB_2) spectrum of 2,6-dibromoaniline (20% solution in CCl_4) are given. The parameters for the single resonance spectrum are $J_{AB} = 7.95 \pm 0.1$ Hz and $|\nu_A - \nu_B| = 89.95 \pm 0.1$ Hz. Double resonance spectra obtained for various strengths and frequencies of irradiation show significant relaxation features as well as marked variations in the inhomogeneity contribution to the various double resonance transitions. Two mechanism of relaxation (i) isotropic random fields and (ii) internal dipole-dipole interactions are considered for detailed analysis. The results of the analysis showed that the relaxation is primarily due to random fields having a ratio of mean square fields at 'A' (position 4) and 'B' (position 3 and 5) protons as 2:1. The random fields at the two 'B' protons are found to be almost completely correlated while those at proton 'A' and any of the 'B' protons practically uncorrelated.

Chapter VI contains the proton relaxation studies in the AB system of 2-bromothiazole (neat liquid). The single resonance parameters are $J_{AB} = 3.55 \pm 0.05$ Hz and $|\nu_A - \nu_B| = 18.8 \pm 0.1$ Hz. The scalar coupling of the protons with N^{14} which has a fast quadrupole relaxation rate, gives rise to broadening in the spectrum and is an important source of relaxation of the protons in this molecule. The analysis of the double resonance spectra obtained for various frequencies and strengths of irradiation leads to some significant information on the scalar coupling parameters including the magnitudes and relative signs of various proton nitrogen coupling constants, as well as the parameters describing the other mechanisms of relaxation in the sample. Conventional relaxation time and linewidth measurements were also used to facilitate the double resonance analysis. The relaxation is found to be primarily through scalar coupling and internal dipole-dipole interaction. The various parameters obtained by the double resonance analysis are for scalar coupling, $J_{AN} \approx 9.7$ Hz, $J_{BN} \approx 2.9$ Hz with J_{AN} and J_{BN} having the same sign and for dipolar interaction $\tau_c \approx 7.0 \times 10^{-12}$ sec.

The thesis has two appendixes, (i) a brief description and listing of a typical Fortran IV computer program and subroutines used in the density matrix calculations and (ii) a reprint of an earlier work by the author on NMR spectra of an ABX_2 spin system and solvent effects on proton-fluorine coupling constants.

Chapter I

INTRODUCTION

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I - INTRODUCTION

IA SPIN RELAXATION-GENERAL

The interaction of a nucleus of magnetic moment $\gamma\hbar\hat{k}$ with a constant magnetic field $H_0\hat{k}$, given by[†]:

$$\mathcal{H} = -\gamma I_z H_0, \quad (I-1)$$

causes a splitting of the $(2I+1)$ energy levels of the nucleus, corresponding to the eigenvalues of I_z . In a macroscopic sample, consisting of an assembly of such nuclei, thermal equilibrium is reached by interactions of the nuclei with each other and with other degrees of freedom in the sample, known as "lattice", giving rise to a Boltzmann distribution of population amongst these levels and a net bulk magnetization M_0 along the direction of H_0 . Transitions between these levels can be induced by a radio-frequency (r.f.) field of appropriate frequency, applied perpendicular to H_0 . The transition probabilities for upward and downward transitions are equal, and since there is an excess of population in the lower levels, this results in a net absorption of energy by the spin system from the r.f. field. This phenomenon is known as nuclear magnetic resonance. The absorption of energy tends to equalise the population of these levels and the rate of

[†] The hamiltonians in this thesis are all expressed in angular frequency units.

absorption is proportional to the population difference. On the other hand, the interaction of the spin system with the other degrees of freedom tends to restore the equilibrium population difference. The latter process is known as the relaxation process. Relaxation is manifest in the process by which a macroscopic sample develops a bulk magnetization $M_0 = \chi_0 H_0$ along the direction of the external field $H_0 \hat{k}$ (where χ_0 is the static susceptibility) and that by which the bulk magnetization in the x-y plane decays to zero.

A description of the relaxation process can be made by studying the time dependence of the components of bulk magnetization $\underline{M}(t)$, the equation of motion for which in the presence of a magnetic field \underline{H} is given by Bloch's phenomenological equation [1]:

$$\frac{d\underline{M}}{dt} = \gamma \underline{M} \times \underline{H} - \hat{i} \frac{M_x}{T_2} - \hat{j} \frac{M_y}{T_2} - \hat{k} \frac{M_z - M_0}{T_1} \quad (I-2)$$

According to this equation, for $\underline{H} = H_0 \hat{k}$, if initially \underline{M} is in any arbitrary direction, the z-component of \underline{M} approaches its equilibrium value M_0 exponentially with a time constant T_1 , known as spin-lattice (or longitudinal) relaxation time and the x and y components of \underline{M} approach their equilibrium value zero exponentially with a time constant T_2 , known as spin-spin (or transverse) relaxation time. A determination of T_1 and T_2 as functions of external parameters can be used to derive information on the

interactions responsible for relaxation. In complicated systems, like liquid samples giving **multiple line spectra under high resolution**, methods like double resonance are used for study of relaxation processes. The present work concerns itself with a study of relaxation processes in coupled spin systems in liquid phase by steady-state double resonance. Before describing the double resonance technique, the particular advantage of the method for the study of relaxation in coupled spin systems in liquids is briefly outlined in the following.

The characteristic features and the methods of experimental study of relaxation are different for different situations. In solids the resonance lines are usually broad due to dipole-dipole interactions, leading to a short spin-spin relaxation time T_2 . The spin-lattice relaxation time T_1 is comparatively long. The spin-spin relaxation may be studied experimentally through linewidths and lineshapes of resonances while, in general, both T_1 and T_2 can be measured by experiments in which the transient response of the spin system to an r.f. perturbation is monitored (e.g. spin-echo method) to determine the relaxation times on the basis of Eq. (I-2).

The situation is rather different, by contrast, in liquids. In liquids the dipole-dipole interactions are averaged out by the rapid molecular motions leading to extremely sharp resonance lines, the widths of which are

primarily determined by the inhomogeneity in the applied magnetic field[†]. Furthermore, the sharpness of the resonance lines in liquids enable the detection of small variations in the electronic environment (chemical shift) and interactions arising from indirect spin-spin coupling in a molecule, which lead to a fine structure in the high resolution n.m.r. spectra. The frequencies and the intensities in such spectra can be described by the hamiltonian, for a single molecule, given by [2]:

$$\mathcal{H}_0 = 2\pi \left[\sum_i v_{oi} I_z(i) + \sum_{i < j} J_{ij} \tilde{I}(i) \cdot \tilde{I}(j) \right], \quad (\text{I-3})$$

where $v_{oi} = -\gamma_i H_0/2\pi$, in which γ_i is the gyromagnetic ratio including the chemical shift of the i^{th} nucleus, and J_{ij} is its spin-spin coupling constant with nucleus j . Transient experiments like the spin-echo method can be used for measurement of relaxation times in liquids if the spectra do not exhibit multiplet structure. When there is multiplet structure, these measurements encounter

+ Exceptions to this statement occur for the resonances of nuclei with spin ≥ 1 , relaxing due to quadrupolar interactions, or for resonances of spin $\frac{1}{2}$ nuclei coupled to either quadrupolar nuclei or nuclei participating in chemical exchange etc.

several difficulties. Separate T_1 and T_2 measurements on each line in a multiplet are not usually possible because the lines are closely spaced, and only an overall effect of a number of lines may be obtained. Furthermore, the description of the relaxation process by single exponentials with time constants T_1 and T_2 , as in Bloch equations, is inadequate. Therefore, for a study of relaxation processes in such cases, one needs a general theory and an experimental method, the results of which are dependent on relaxation processes. Wangsness and Bloch [3] and Bloch [4] have given a density-matrix theoretical description of the phenomenon of nuclear induction. The density-matrix treatment is quite general and suitable for description of relaxation effects in a variety of systems. Double resonance experiments, the results of which are interpreted by the density-matrix theory, meet the above requirements for relaxation studies in coupled spin systems in liquids.

IB DOUBLE RESONANCE

The double-resonance experiments consist of irradiation of one of the transitions in the spectrum by a strong r.f. field and simultaneous observation of the remaining parts of the spectrum by another weak r.f. field. The principle of this method is based on the fact that the strong r.f. field competes with the processes of relaxation in the spin system, thereby causing a variety of effects viz. changes in populations and lifetimes of the energy

levels which in turn are reflected as changes in intensities and linewidths in the double-resonance spectrum [4]. The quantitative details of these features depend on the relaxation processes in the spin system. Information on the relaxation processes is then obtained by comparing the observed features with those calculated for various relaxation mechanisms.

Strong irradiation also mixes various eigenstates of the spin hamiltonian (Eq. I-3), giving rise to new transitions and shifts in frequencies of single resonance transitions [4]. These features are implicitly included in a detailed analysis of double-resonance spectra even though they do not depend on relaxation, and can be completely understood by a diagonalization of the spin hamiltonian including the irradiating field, in a frame rotating at the irradiating frequency [5 a].

A density-matrix description of the phenomenon of nuclear induction as formulated by Bloch [4] and Redfield [6], and given by Abragam [7] and Hubbard [8], is capable of describing all the effects of the double resonance experiments including, in particular, the relaxation effects. In this formalism the dynamical behaviour of the spin system is described by rewriting the general equation of motion of the density matrix, using second order perturbation theory for the spin-lattice interaction. This results in differential equations for the various elements of the density matrix, which include

the effects of relaxation through the elements of a general "relaxation matrix"[6]. The various relaxation matrix elements contain, for a multilevel system, the information implied in T_1 and T_2 of Bloch's phenomenological equation (I-2). The results of double-resonance experiments are then described through changes produced in the density matrix due to irradiation. This involves a consideration of the complete relaxation matrix. A calculation of these changes for various probable relaxation mechanisms is then compared with the observed features in a steady-state double-resonance experiment. This method thus avoids some of the theoretical ambiguities and experimental difficulties in T_1 and T_2 measurements, mentioned earlier. Furthermore, these experiments provide an example in which a detailed consideration of the density matrix formalism is required and thus form an experimental test for the theory.

In the following some of the previous work on the study of relaxation in coupled spin systems by the double-resonance technique is briefly described in order to discuss the motivation and the nature of the work presented in this thesis.

Baldeschwieler [5] gave a detailed method of calculation of relaxation effects in double resonance based on the density-matrix formalism of Bloch [4] and Redfield [6]. This method was applied to the proton double resonance in the single spin system of CHCl_3 and some

discrepancies were noticed between experiment and theory. This method of analysis was later on re-examined by Nageswara Rao [9] and a similar but somewhat improved method was suggested. It was shown that the approximation originally proposed by Bloch [4] for systems with weak relaxation, for the analysis of the double resonance spectra obtained under conditions of strong irradiation, is applicable even when the frequency of irradiation is very close to a single resonance transition. A reinvestigation of proton double resonance in CHCl_3 , on this basis, removed the discrepancies between the theory and the experiment for the single spin $\frac{1}{2}$ case [10].

Nageswara Rao, Baldeschwieler and Anderson [11], used the above method to analyse the results of steady-state frequency-sweep double resonance experiments on a strongly coupled two spin system (AB) formed by the protons in 2-bromo-5-chlorothiophene, under conditions of strong irradiation. The validity of Bloch approximation for strong irradiation spectra has been varified in this analysis and furthermore it was possible to clearly distinguish between different relaxation mechanisms on the basis of a comparison between the observed and the calculated relative intensities in the double resonance spectra. The relaxation in this molecule was found to be predominantly due to correlated external random fields. Wakefield and Memory [12] recently made similar studies on an AB and an ABX type of spin system, using Bloch approximation,

and concluded that the correlated random fields fit their spectra best. Steady-state double resonance experiments have also been performed on an AB spin system by Matsuoka and Kakiuchi [13], to obtain quantitative information on the contribution to relaxation for various intramolecular and intermolecular interactions and concluded that a single exponential cannot be used to describe various relaxation rates.

Noggle performed transient as well as steady-state double resonance experiments on the AB spin system of 2,3-dibromothiophene [14]. The transient experiments involved a periodic observation of recovery of single resonance intensity after the saturating r.f. field is turned off. He also examined the correlations between external random fields and concluded that both internal dipole-dipole interaction and external random fields with partial correlation are responsible for relaxation in this molecule. Kuhlmann and Baldeschwieler [15] made similar studies in difluoroethylenes. These authors used low strengths of irradiation such that line splittings and shifts do not occur and only intensity changes in the single resonance spectra are observed (generalised Overhauser effect [4]). The spectra were analysed by using external random field model for various relaxation mechanisms. It was concluded that spin-rotation interaction is responsible for relaxation between states of different symmetry. In this case information regarding the relaxation rate of fluorine

could be obtained while observing only proton resonance.

Steady-state double resonance studies have been extended by Nageswara Rao and Lessinger [16], to weakly coupled systems containing a large number of spins. It was shown that if the interactions causing relaxation in such systems satisfy certain symmetry requirements, it is possible to obtain quantitative information on the relaxation by assuming a random field model. The double resonance experiments were performed in ethylfluoride and the results indicated that the relaxation of fluorine is approximately four times as efficient as that of protons in this molecule.

Closely connected with the studies mentioned above are some heteronuclear double resonance experiments in the AX spin systems of $C^{13}-H^1$ in chloroform [17] and that of H^1-D^2 in gaseous HD [18]. Significant relaxation information has been obtained by using the density-matrix analysis for these systems. Interesting extensions of the steady-state and transient double resonance experiments have been made by Gordon and Baldeschwiler [19,20] and Gordon [21] in which the observing and the irradiating r.f. fields are periodically pulsed. Double resonance experiments have also been performed in liquid mixtures (intermolecular Overhauser effect) [22].

These experiments clearly demonstrate that the double resonance experiments coupled with density-matrix

analysis are capable of yielding worthwhile information on the relaxation processes in different types of spin systems and under a variety of experimental conditions.

IC PRESENT WORK

The work presented in this thesis, on coupled spin systems, is undertaken to study the systematics of the double resonance method and to obtain quantitative information on the various mechanisms of proton relaxation. The scope of the present work is restricted to steady-state double resonance experiments. The work is based on the study of proton-proton double resonance spectra of (1) AB_2 spin system formed by the ring protons of 2,6-dibromoaniline studied as a 20 per cent solution in CCl_4 and (2) AB spin system formed by the protons in 2-bromothiazole studied as a neat liquid. Double resonance spectra were obtained, in each case, by irradiating each one of the single resonance transitions over a wide range of strengths of irradiation.

From the analysis of the AB_2 spin system the following points have emerged: it is found that an explicit consideration of the effect of inhomogeneity of the magnetic field is of considerable importance in the determination of quantitative information on relaxation from double resonance spectra. Freeman and Anderson [23] have shown that the inhomogeneity contributes, in general, different widths to different transitions in a double

resonance spectrum. In the present work a method has been suggested to include this in the density matrix analysis of double resonance spectra and this led to a reliable estimate of the relaxation parameters. This effect has been overlooked in earlier studies of relaxation by double resonance [11-14,16,18,24]. Secondly, it is shown in this work that it is often useful to study the double resonance spectra over a wide range of strengths of irradiation. This is due to the fact that the solutions of the density-matrix equations for high strengths of irradiation are determined by the relative values of relaxation matrix elements while those for low strengths of irradiation depend on their absolute values. This distinction is of considerable value in distinguishing between different mechanisms.

Two relaxation processes (i) external isotropic random fields and (ii) internal dipole-dipole interactions, along with various probable degrees of correlation in each case, were considered for a detailed analysis of relaxation effects in the AB_2 spin system. The correlation constants for the isotropic random fields are defined to include the possibility of complete correlation accompanied by different mean square fields. The analysis led to the conclusion that the relaxation in the spin system is primarily due to external random fields with a ratio 2:1 for the mean square fields at the "A" proton (position 4) to those at the "B" protons (positions 3 and 5). The random fields at the two

'B' proton sites are found to be highly correlated while those at the 'A' proton site and any of the 'B' proton sites are completely uncorrelated.[†]

In the AB spin system of 2-bromothiazole scalar coupling of protons with N¹⁴, which has a fast quadrupole relaxation, was found to modify the process of relaxation of the former to a large extent. This coupling causes significant broadening in the proton spectrum of this molecule. The double resonance study yielded information on the various parameters describing the scalar coupling interactions viz., the magnitudes and relative sign of the proton-N¹⁴ coupling constants. The scalar coupling interaction was also examined in some detail and the conditions under which it can be treated only as a mechanism for relaxation are discussed. It is found that under the conditions of the experiment the scalar coupling interaction contributes significantly only to spin-spin relaxation, so that the contact of the spin system with the lattice should be through other interactions. A detailed double resonance analysis for both 'high' and 'low' amplitudes of irradiation cases led to the conclusion that the internal dipole-dipole interactions along with the scalar coupling account for the spin relaxation in this molecule. A graphical method for interpretation of the

† The results of this study are published in a paper by Anil Kumar and B.D. Nageswara Rao, Molec. Phys., 15, 377 (1968).

spectra with 'low' amplitudes of irradiation is adopted for this analysis.[†]

It is often convenient to use the model of an isotropic random field for the analysis of relaxation effects in the double resonance studies. This is because this interaction is linear in the spin operators I_x , I_y and I_z and the lattice variables and possesses isotropy. This model represents the overall affect of various intramolecular and intermolecular interactions explicit consideration of which is rather involved. As part of this work, the conditions under which different mechanisms can be approximated by a random-field model are examined. It is shown that under conditions normally used in experiments, several of the mechanisms can be approximated by such a model.

The experiments were performed at room temperature and by frequency-sweep method. The experimental arrangement is similar to the standard arrangements used in literature [23,25] with some minor modifications arising from the particular apparatus used. This arrangement was set-up and was used along with a Varian HR-100 n.m.r. spectrometer.

The plan of presentation of the thesis is as follows. The notation and the density-matrix method used in this work are given in Sec. IIA. The treatment of inhomogeneity and its contribution to single and double

[†] The results of this study form part of a paper by Anil Kumar, N. Rama Krishna and B.D. Nageswara Rao, Molec. Phys., 1969 (in press).

resonance spectra are given in Sec. IIB. The solutions of the density-matrix equations for different strengths of irradiation are discussed in Sec. IIC along with a graphical method for interpretation of spectra for 'low' strengths of irradiation. Various relaxation mechanisms are listed in Sec. IIIA, and the conditions under which they can be approximated by a random field are examined in Sec. IIIB. Chapter III also contains a discussion of the conditions under which scalar coupling can be treated only as a mechanism of relaxation. The details of the experimental arrangement for frequency-sweep double-resonance experiments are given in Chapter IV. Chapter V contains the results of double resonance experiments on the AB_2 spin system of 2,6-dibromoaniline and their analysis. Double resonance spectra in this molecule showed significant relaxation features and marked variations in the contribution of inhomogeneity to the linewidths. These features are discussed in detail. Chapter VI contains the results of the double-resonance experiments and analysis of the relaxation effects in the AB spin system of 2-bromothiazole. The conclusions and results of the work are summarized in the end. There are two appendixes to the thesis (i) a brief discussion and a listing of a typical computer program used in the density-matrix analysis and (ii) a reprint copy of an earlier work on solvent effects on coupling constants, by the author.

Chapter II

THEORY

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II - THEORY

IIA BASIC DENSITY MATRIX FORMALISM

1. Equation of Motion

The density-matrix method of analysis of double resonance spectra given recently by Baldeschwieler [5] and Nageswara Rao [9], based on the formalism of Bloch [4] and Redfield [6], (also discussed by Abragam [7]), is discussed briefly in this section. This presents the basic assumptions involved in the theory and the notation to be used in the later sections.

The equation of motion of the density matrix of the total system (including the nuclear spin system, the lattice and their interaction), in Schrödinger representation, is given by:

$$\frac{d\rho}{dt} = -i[\mathcal{H}(t) + \mathcal{L} + \mathcal{H}', \rho], \quad (\text{II-1})$$

where $\mathcal{H}(t)$ is the spin hamiltonian which is time dependent because of the observing and irradiating r.f. fields, \mathcal{L} is the hamiltonian of the lattice and \mathcal{H}' is the spin-lattice interaction.

Transforming Eq. (II-1) into an interaction representation by defining :

$$\left. \begin{aligned} \rho^I &= U(t) e^{i\mathcal{L}t} \rho e^{-i\mathcal{L}t} U^{-1}(t) \\ \mathcal{H}'^I(t) &= U(t) e^{i\mathcal{L}t} \mathcal{H}' e^{-i\mathcal{L}t} U^{-1}(t) \end{aligned} \right\} \quad (\text{II-2})$$

where $U(t) = U(t,0)$ obeys the differential equation

$$\frac{dU(t)}{dt} = i U(t) \mathcal{H}(t) \quad (\text{II-3})$$

gives:

$$\frac{d\mathcal{S}^I}{dt} = -i[\mathcal{H}'^I(t), \mathcal{S}^I]. \quad (\text{II-4})$$

Equation (II-4) solved in two successive approximations leads to:

$$\begin{aligned} \frac{d\mathcal{S}^I}{dt} = & -i[\mathcal{H}'^I(t), \mathcal{S}^I(0)] - \int_0^t [\mathcal{H}'^I(t), \\ & [\mathcal{H}'^I(t-\tau), \mathcal{S}^I(0)]]d\tau. \end{aligned} \quad (\text{II-5})$$

A spin density matrix σ is defined by:

$$\sigma^I(t) = \text{Tr}_f \{ \mathcal{S}^I(t) \}, \quad (\text{II-6})$$

where

$$\sigma^I(t) = U(t) \sigma(t) U^{-1}(t) \quad (\text{II-7})$$

and $\text{Tr}_f \{ \}$ represents the trace over lattice states.

Equation (II-5) is solved with the following assumptions:

i) The time $t = 0$ is so chosen that the system is in thermal equilibrium at that time. The lattice is assumed to have a large heat capacity and to remain always in thermal equilibrium, $\mathcal{S}^I(0)$ is then factorizable into spin and lattice parts:

$$\xi^I(0) = \lambda^I(0) \sigma^I(0), \quad (\text{II-8})$$

where $\lambda^I(0) = \lambda(0)$ and $\sigma^I(0) = \sigma(0)$ are the equilibrium density-matrices at the lattice temperature for the lattice and spin parts respectively.

ii) $\mathcal{H}'(t) = e^{i\mathcal{H}t} \mathcal{H}' e^{-i\mathcal{H}t}$, known as relaxation hamiltonian, is a random operator uncorrelated with $\sigma(0)$. The trace over the lattice states will then give zero for the first term on R.H.S. of Eq. (II-5).

iii) The upper limit of integration in Eq. (II-5) can be extended to infinity if $t \gg \tau_c$, where τ_c is the correlation time for time dependence of $\mathcal{H}'(t)$. While $t \gg \tau_c$ it should, however, be short enough to satisfy the perturbation expansion of Eq. (II-5). For short correlation, $\sigma^I(0)$ in the second term on the R.H.S. of Eq. (II-5) may be replaced by $\sigma^I(t)$.

iv) The time independent part \mathcal{H}_0 of $\mathcal{H}(t)$ is such that $\hbar \mathcal{H}_0/kT \gg 1$ (high temperature approximation). This allows a replacement of $\sigma^I(t)$ by $(\sigma^I(t) - \sigma(0))$ in the second term on the R.H.S. of Eq. (II-5), while performing the operation $\text{Tr}_f\{ \}$.

Transforming back to Schrödinger representation and noting that in liquids, where the lattice motion may be adequately described classically, the operation of trace after multiplying with $\lambda(0)$ can be replaced by a classical ensemble average [26], denoted by $\langle \rangle_{\text{av}}$, one obtains:

$$\frac{d\sigma}{dt} = -i[\mathcal{H}(t), \sigma] - \int_0^\infty \left[\mathcal{H}'(t), [U(t-\tau, t) \mathcal{H}'(t-\tau) U^{-1}(t-\tau, t), \sigma(t) - \sigma(0)] \right] d\tau, \quad (\text{II-9})$$

where

$$\sigma(0) = \sigma_0 = \frac{1}{N} \left(1 - \frac{\hbar \mathcal{H}_0}{kT} \right) = \frac{1}{N} - q \mathcal{H}_0, \quad (\text{II-10})$$

N is the number of spin states and $q = \hbar/NkT$.

At this point one of the following two assumption is usually made, depending on how short τ_c is:

(a) "Extreme narrowing" :- This assumption requires

$|\mathcal{H}_0 \tau_c| \ll 1$. If it is valid, $U(t-\tau, t)$ of Eq. (II-9) becomes unity and the spectral densities (to be defined later) become independent of frequency [ref. 7, p. 280].

(b) "Non-viscous liquid" approximation. If τ_c is not short enough to satisfy (a), it is most likely that

$\sum_k \mathcal{H}_k(t) \tau_c \ll 1$, where the summation k is over all the time-dependent parts of spin hamiltonian (In double resonance ^{these are due to} the observing and irradiating r.f. fields, and In all the cases of present interest, the strengths of these fields are very much smaller than \mathcal{H}_0 [ref. 7, p. 515]). This leads to $U(t-\tau, t) = \exp(-i \mathcal{H}_0 \tau)$ in Eq. (II-9).

Although the exact form for $\mathcal{H}'(t)$ depends upon the particular interaction between the spin system and the lattice, it can, in general, be expressed as:

$$\mathcal{H}'(t) = \sum_q (-1)^q A^{(q)} F^{(-q)}(t), \quad (\text{II-11})$$

where $A^{(q)}$ are spin operators and $F^{(q)}(t)$ are random functions of lattice variables expressed in irreducible form. The hermiticity of $\mathcal{H}'(t)$ requires:

$$F^{(q)*}(t) = (-1)^q F^{(-q)}(t) \text{ and } A^{(q)\dagger} = (-1)^q A^{(-q)}. \quad (\text{II-12})$$

This form for $\mathcal{H}'(t)$ leads to the simplification:

$$\left\langle F^{(q)}(t) F^{(q')*}(t') \right\rangle_{av} = \delta_{qq'} \left\langle F^{(q)}(t) F^{(q)*}(t') \right\rangle_{av} \quad (\text{II-13})$$

known as "secular approximation", which arises from the fact that the "non-secular" terms ($q \neq q'$) vary rapidly with time and give zero on averaging over the ensemble[4]. Using Eqs. (II-11) - (II-13) and the "non-viscous liquid" approximation, Eq. (II-9) becomes [26]:

$$\frac{d\sigma}{dt} = -i[\mathcal{H}(t), \sigma] - \int_0^\infty \left\langle [\mathcal{H}'(t), [\mathcal{H}'_a(t-\tau), \sigma - \sigma_0]] \right\rangle_{av} d\tau, \quad (\text{II-14})$$

where

$$\mathcal{H}'_a(t-\tau) = \sum_q (-1)^q A^{(q)}(\tau) F^{(-q)}(t-\tau), \quad (\text{II-15})$$

in which

$$A^{(q)}(\tau) = e^{-i 2\pi\tau v_0 \sum_j I_z(j)} A^{(q)} e^{i 2\pi\tau v_0 \sum_j I_z(j)}, \quad (\text{II-16})$$

where $\nu_0 = -\gamma H_0/2\pi$, and in writing Eq. (II-16) the coupling constants and the chemical shifts have been neglected compared to Larmor frequencies in \mathcal{H}_0 . In the "extreme-narrowing" limit the equation of motion of σ , Eq. (II-9), becomes [9]:

$$\frac{d\sigma}{dt} = -i[\mathcal{H}(t), \sigma] - \left\langle \tau_c [\mathcal{H}'(t), [\mathcal{H}'(t), \sigma - \sigma_0]] \right\rangle_{av} \quad (\text{II-17})$$

2. Double Resonance - Rotating Coordinate Transformation

The spin hamiltonian:

$$\mathcal{H}(t) = \mathcal{H}_0 + \mathcal{H}_1(t) + \mathcal{H}_2(t) \quad (\text{II-18})$$

consists of a time-independent part \mathcal{H}_0 , defined in Eq.(I-3), and interactions of the spins with a weak observing r.f. field $\mathcal{H}_1(t)$ and a strong irradiating r.f. field $\mathcal{H}_2(t)$, given by:

$$\mathcal{H}_k(t) = D_{k+} \exp(i\omega_k t) + D_{k-} \exp(-i\omega_k t), \quad (\text{II-19})$$

where

$$D_{\pm} = \pi \sum_i v_{\pm i} I_{\pm}(i) \quad (\text{II-20})$$

and

$$v_{ki} = -\gamma_i H_k / 2\pi \quad k = 1, 2 \quad (\text{II-21})$$

in which J_{ij} and v_{ki} are expressed in Hz, and $\underline{H}_1 = H_1 \cos \omega_1 t \hat{i} - H_1 \sin \omega_1 t \hat{j}$ is the observing r.f. field and $\underline{H}_2 = H_2 \cos \omega_2 t \hat{i} - H_2 \sin \omega_2 t \hat{j}$ is the irradiating r.f. field.

Transforming to a coordinate frame rotating at the frequency $(-\omega_2 \hat{k})$ of the irradiating field \underline{H}_2 through the operator

$$T = \exp(-i\omega_2 t \sum_j I_z(j)) \quad (\text{II-22})$$

and noting that:

$$\begin{aligned} \tilde{\mathcal{H}}_2 &= T \mathcal{H}_2 T^{-1} = D_{2+} + D_{2-} , \\ \tilde{\mathcal{H}}_1(t) &= D_{1+} \exp(i\omega' t) + D_{1-} \exp(-i\omega' t) , \\ [\mathcal{H}_0, T] &= 0 ; [\sigma_0, T] = 0 , \end{aligned} \quad (\text{II-23})$$

where \sim denotes operators in the rotating frame and $\omega' = \omega_1 - \omega_2$, Eq. (II-14) gives:

$$\frac{d\tilde{\sigma}}{dt} = -i[\mathcal{H}_0^R + \tilde{\mathcal{H}}_1(t), \tilde{\sigma}] - \int_0^\infty \left\langle [\mathcal{H}(t), [\mathcal{H}_a'(t-\tau), \tilde{\sigma} - \sigma_0]] \right\rangle_{av} d\tau \quad (\text{II-24})$$

$$= -i[\mathcal{H}_0^R + \tilde{\mathcal{H}}_1(t), \tilde{\sigma}] - \Gamma(\tilde{\sigma} - \sigma_0) , \quad (\text{II-25})$$

where

$$\begin{aligned} \mathcal{H}_0^R &= \mathcal{H}_0 + \omega_2 \sum_i I_z(i) + \tilde{\mathcal{H}}_2 \\ &= 2\pi \left[\sum_i A_i I_z(i) + \sum_{i < j} J_{ij} \underline{I}(i) \cdot \underline{I}(j) \right] + (D_{2+} + D_{2-}) , \end{aligned} \quad (\text{II-26})$$

in which

$$A_i = v_{oi} + \omega_2/2\pi . \quad (\text{II-27})$$

$\overline{(\tilde{\sigma} - \sigma_0)}$ is the relaxation term defined by its matrix elements in a basis in which \mathcal{H}_0^R is diagonal if the solution is obtained in the rotating frame through Eq. (II-24).

$\overline{(\sigma - \sigma_0)}$ will similarly be the relaxation term defined by its matrix elements in a basis in which \mathcal{H}_0 is diagonal if the solution is obtained in the laboratory frame through Eq. (II-14). In general in a basis $\alpha, \alpha' \dots$

$$\overline{_{\alpha\alpha'}(\sigma - \sigma_0)} = - \sum_{\beta\beta'} R_{\alpha\alpha', \beta\beta'} (\tilde{\sigma} - \sigma_0)_{\beta\beta'}, \quad (\text{II-28})$$

where

$$R_{\alpha\alpha', \beta\beta'} = \frac{1}{2} [J_{\alpha\beta\alpha'\beta'} + J_{\beta'\alpha'\beta\alpha} - \delta_{\alpha\beta} \sum_{\gamma} J_{\gamma\alpha'\gamma\beta'} - \delta_{\alpha'\beta'} \sum_{\gamma} J_{\gamma\alpha\gamma\beta}], \quad (\text{II-29})$$

in which

$$J_{\alpha\beta\alpha'\beta'} = \int_{-\infty}^{+\infty} \left\langle \alpha \left| \mathcal{H}'(t) \right| \beta \right\rangle \left\langle \alpha' \left| \mathcal{H}'_a(t-\tau) \right| \beta' \right\rangle^* \rangle_{\text{av}} d\tau. \quad (\text{II-30})$$

In writing the spectral densities $J_{\alpha\beta\alpha'\beta'}$, in this form, the imaginary part, which is usually small, is neglected [ref. 7, p. 279][†].

The hermiticity of $\mathcal{H}'(t)$ yields [9]:^{††}

[†] This term is zero for the "extreme-narrowing" assumption.

^{††} These symmetry relations are obtained for "extreme narrowing" and will hold for "non-viscous liquid" approximation if the chemical shifts and coupling constants are neglected compared to Larmor frequencies in writing the Eq.(II-16).

$$J_{\alpha\beta\alpha'\beta'} = J_{\beta\alpha\beta'\alpha'} = J_{\alpha'\beta'\alpha\beta} = J_{\beta'\alpha'\beta\alpha} , \quad (\text{II-31})$$

giving:

$$R_{\alpha\alpha'\beta\beta'} = R_{\alpha'\alpha\beta'\beta} = R_{\beta\beta'\alpha\alpha'} = R_{\beta'\beta\alpha'\alpha} , \quad (\text{II-32})$$

and

$$\sum_{\alpha} R_{\alpha\alpha\beta\beta'} = 0 . \quad (\text{II-33})$$

Using Eqs. II-(11-13), (II-15) and (II-16) we get for Eq. (II-30) under "non-viscous liquid" approximation:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = \sum_q \int_{-\infty}^{+\infty} \left\{ \left\langle F^{(q)}(t) F^{(q)*}(t-\tau) \right\rangle_{av} \left\langle \alpha | A^{(-q)} | \beta \right\rangle \left\langle \alpha' | A^{(-q)}(\tau) | \beta' \right\rangle^* \right\} d\tau \quad (\text{II-34})$$

and for "extreme-narrowing" approximation:

$$J_{\alpha\beta\alpha'\beta'}^{en} = 2\tau_c \sum_q \left\langle |F^{(q)}|^2 \right\rangle_{av} \left\langle \alpha | A^{(-q)} | \beta \right\rangle \left\langle \alpha' | A^{(-q)} | \beta' \right\rangle . \quad (\text{II-35})$$

3. Solution of Equation of Motion

Equation (II-25) is solved in two steps, first by determining the deviation $\chi(t)$ caused by the irradiating r.f. field $\mathcal{H}_2(t)$ in the unperturbed spin density matrix σ_0 , and then by obtaining the deviation $\eta(t)$ caused by the observing r.f. field $\mathcal{H}_1(t)$ on the resulting system. The total spin density matrix, including the effect of two r.f. fields, is then expressed as:

$$\sigma(t) = \sigma_0 + \chi(t) + \eta(t). \quad (\text{II-36})$$

In writing this expression, linear superposition of the effects of the irradiating and the observing fields on the density matrix is assumed.

In the rotating coordinate system:

$$\tilde{\sigma}(t) = \sigma_0 + \tilde{\chi} + \tilde{\eta}(t), \quad (\text{II-37})$$

where $\tilde{\chi}$ is independent of time, since $\tilde{\mathcal{H}}_2$ is independent of time in the rotating frame.

(a) Effect of Irradiation:- Setting $\tilde{\mathcal{H}}_1(t) = 0$; $\tilde{\eta}(t)=0$, in the first step of ^{the} solution, Eq. (II-25) becomes in the steady-state:

$$[\mathcal{H}_0^R, \sigma_0 + \tilde{\chi}] - i \overline{(\tilde{\chi})} = 0. \quad (\text{II-38})$$

Using Eqs. (II-10) and (II-26) and neglecting the chemical shift between irradiated nuclei compared to their Larmor frequency one gets on taking the matrix elements of Eq.(II-38) in the $\alpha, \alpha' \dots$ basis (such that $\mathcal{H}_0^R |\alpha\rangle = E_\alpha |\alpha\rangle$):

$$(E_\alpha - E_{\alpha'}) \tilde{\chi}_{\alpha\alpha'} + i \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'} \tilde{\chi}_{\beta\beta'} = -(2\pi q v_0)(\pi v_2) \sum_j [I_+(j) - I_-(j)]_{\alpha\alpha'}. \quad (\text{II-39})$$

Since the density matrix is hermitian $\text{Re}(\tilde{\chi}_{\alpha\alpha'}) = \text{Re}(\tilde{\chi}_{\alpha'\alpha})$ and $\text{Im}(\tilde{\chi}_{\alpha\alpha'}) = -\text{Im}(\tilde{\chi}_{\alpha'\alpha})$ and the diagonal elements of

$\tilde{\chi}$ are real. Separating the real and imaginary parts of Eq. (II-39) gives for $\alpha \neq \alpha'$:

$$\begin{aligned} (E_\alpha - E_{\alpha'}) \operatorname{Re}(\tilde{\chi}_{\alpha\alpha'}) - \sum_{\beta < \beta'} (R_{\alpha\alpha'\beta\beta'} - R_{\alpha\alpha'\beta'\beta}) \operatorname{Im}(\tilde{\chi}_{\beta\beta'}) \\ = -(2\pi q v_0)(\pi v_2) \sum_j [I_+(j) - I_-(j)]_{\alpha\alpha'}, \quad (\text{II-40}) \end{aligned}$$

$$\begin{aligned} (E_\alpha - E_{\alpha'}) \operatorname{Im}(\tilde{\chi}_{\alpha\alpha'}) + \sum_{\beta < \beta'} (R_{\alpha\alpha'\beta\beta'} + R_{\alpha\alpha'\beta'\beta}) \operatorname{Re}(\tilde{\chi}_{\beta\beta'}) \\ + \sum_{\beta} R_{\alpha\alpha'\beta\beta} (\tilde{\chi}_{\beta\beta}) = 0, \quad (\text{II-41}) \end{aligned}$$

and for $\alpha = \alpha'$:

$$2 \sum_{\beta < \beta'} R_{\alpha\alpha\beta\beta'} \operatorname{Re}(\tilde{\chi}_{\beta\beta'}) + \sum_{\beta} R_{\alpha\alpha\beta\beta} \tilde{\chi}_{\beta\beta} = 0. \quad (\text{II-42})$$

Equations (II-40) to (II-42) form a set of N^2 simultaneous equations in the matrix elements of $\tilde{\chi}$, of which the N equations given by Eq. (II-42) are linearly dependent. Using the condition $\operatorname{Tr} \tilde{\sigma} = \operatorname{Tr} \sigma_0 = 1$, gives:

$$\sum_{\beta} \tilde{\chi}_{\beta\beta} = 0, \quad (\text{II-43})$$

and a unique solution for the complete $\tilde{\chi}$ matrix can be obtained by replacing one of the equation in (II-42) by Eq. (II-43). Further simplification of the set of Eqs. (II-40) to (II-43) is possible depending on the strength of irradiation. This aspect will be discussed in Sec. IIC.

(b) Effect of Observing Field:- The deviation in the spin density matrix $(\sigma_0 + \tilde{\chi})$ due to observing r.f. field $\tilde{\mathcal{H}}_1(t)$, given by $\tilde{\eta}(t)$, is obtained using Eqs. (II-25), (II-37) and (II-38) as:

$$\begin{aligned} \frac{d\tilde{\eta}(t)}{dt} = & -i [\mathcal{H}_0^R, \tilde{\eta}(t)] - i [\tilde{\mathcal{H}}_1(t), \sigma_0 + \tilde{\chi} + \tilde{\eta}(t)] \\ & - \Gamma(\tilde{\eta}(t)). \end{aligned} \quad (\text{II-44})$$

A steady-state solution for $\tilde{\eta}(t)$ for small values of $H_1(t)$, small enough not to cause any saturation effects, is obtained by assuming that the diagonal elements of $\tilde{\eta}(t)$ are zero and that the off-diagonal elements have a time dependence given by:

$$\tilde{\eta}_{\alpha\alpha'}(t) = Y_{\alpha\alpha'}^+ e^{i\omega't} + Y_{\alpha\alpha'}^- e^{-i\omega't} \quad (\text{II-45})$$

Using the hermiticity for $\tilde{\eta}(t)$, substituting (II-45) in Eq. (II-44), collecting terms varying as $\exp(i\omega't)$, $\exp(-i\omega't)$ and constant in time, and separating the real and imaginary parts give a set of linear simultaneous equations in the matrix elements of $\tilde{\eta}(t)$. If ω_1 is not very close to ω_2 and for small $H_1(t)$, these equations simplify to give [9]:

$$\begin{aligned} (\pm\omega' + E_\alpha - E_{\alpha'}) \operatorname{Re}(Y_{\alpha\alpha'}^\pm) + \sum_{\beta < \beta'} R_{\alpha\alpha'\beta\beta'} \operatorname{Im}(Y_{\beta\beta'}^\pm) = \\ -[D_{1\pm}, (\operatorname{Re}\tilde{\chi} + \sigma_0)]_{\alpha\alpha'} \end{aligned} \quad (\text{II-46})$$

$$\begin{aligned}
(\pm \omega' + E_\alpha - E_{\alpha'}) \operatorname{Im}(Y_{\alpha\alpha'}^\pm) - \sum_{\beta < \beta'} R_{\alpha\alpha', \beta\beta'} \operatorname{Re}(Y_{\beta\beta'}^\pm) = \\
- [D_{1\pm}, \operatorname{Im} \tilde{\chi}]_{\alpha\alpha'}, \quad (II-47)
\end{aligned}$$

in which the upper sign is important if $(\omega' + E_\alpha - E_{\alpha'})$ is small and the lower sign if $(-\omega' + E_\alpha - E_{\alpha'})$ is small.

Only one of the off-diagonal elements of $\tilde{\eta}(t)$, corresponding to the transition being observed, is important at a time if there are no overlapping transitions present in the double resonance spectrum. One then obtains:

$$\operatorname{Re}(Y_{\alpha\alpha'}^\pm) = \frac{-(\pm \omega' + E_\alpha - E_{\alpha'}) [D_{1\pm}, (\operatorname{Re} \tilde{\chi} + \sigma_0)]_{\alpha\alpha'} + R_{\alpha\alpha', \alpha\alpha'} [D_{1\pm}, \operatorname{Im} \tilde{\chi}]_{\alpha\alpha'}}{(\pm \omega' + E_\alpha - E_{\alpha'})^2 + R_{\alpha\alpha', \alpha\alpha'}^2}, \quad (II-48)$$

$$\operatorname{Im}(Y_{\alpha\alpha'}^\pm) = \frac{-R_{\alpha\alpha', \alpha\alpha'} [D_{1\pm}, (\operatorname{Re} \tilde{\chi} + \sigma_0)]_{\alpha\alpha'} - (\pm \omega' + E_\alpha - E_{\alpha'}) [D_{1\pm}, \operatorname{Im} \tilde{\chi}]_{\alpha\alpha'}}{(\pm \omega' + E_\alpha - E_{\alpha'})^2 + R_{\alpha\alpha', \alpha\alpha'}^2}. \quad (II-49)$$

4. Signal Intensity

The macroscopic expectation value of an operator is given by a trace of the product of the operator with the density matrix, and therefore the signal in a nuclear induction experiment is given by [5,9]:

$$\begin{aligned}
S &= -K' \frac{d}{dt} \sum_i \gamma_i \text{Tr} \{ I_y(i) \sigma \} = -\frac{K'}{2i} \frac{d}{dt} \sum_i \gamma_i \text{Tr} \{ I_+(i) \sigma - I_-(i) \sigma \} \\
&= -\frac{K'}{2i} \frac{d}{dt} \sum_i \gamma_i \text{Tr} \left\{ I_+(i) e^{i\omega_2 t} \tilde{\sigma} - I_-(i) e^{i\omega_2 t} \tilde{\sigma} \right\}
\end{aligned}
\tag{II-50}$$

where K' is a proportionality constant. The diagonal elements of $\tilde{\sigma}$ which are time independent contribute signals at ω_2 , and the off-diagonal elements at $(\pm\omega' + \omega_2) = \omega_1$ ~~or~~ ^{and} $(-\omega_1 + 2\omega_2)$. The intensity of a transition at ω_1 , in the absorption mode, is given by:

$$S_{\alpha\alpha'}^{\pm} = \mp K \omega_1 \sum_i \gamma_i (I_{\pm}(i))_{\alpha\alpha'} \text{Im}(Y_{\alpha\alpha'}^{\pm}) \sin \omega_1 t \tag{II-51}$$

$$= \mp K \omega_1 \sum_i \gamma_i (I_{\pm}(i))_{\alpha\alpha'} \sin \omega_1 t$$

$$\begin{aligned}
&\times \left[\frac{-R_{\alpha\alpha',\alpha\alpha'} [D_{1\pm}, (\text{Re } \tilde{\chi} + \sigma_0)]_{\alpha\alpha'} - (\pm\omega' + E_{\alpha} - E_{\alpha'}) [D_{1\pm}, \text{Im } \tilde{\chi}]_{\alpha\alpha'}}{(\pm\omega' + E_{\alpha} - E_{\alpha'})^2 + R_{\alpha\alpha',\alpha\alpha'}^2} \right],
\end{aligned}
\tag{II-52}$$

The second term in the numerator of Eq. (II-52) is negligible if Bloch approximation holds (to be discussed in Sec IIC), and the signal $S_{\alpha\alpha'}^{\pm}$ becomes a lorentzian with half-width $R_{\alpha\alpha',\alpha\alpha'}$ at half-height. The peak signal intensity $S_{\alpha\alpha'}^{\pm p}$ is given by:

$$S_{\alpha\alpha'}^{\pm, p} = \frac{\pm K(\omega_1, H_1) \sum_i \gamma_i^2 (I_{\pm}(i))_{\alpha\alpha'} [I_{\pm}(i), (\text{Re } \tilde{\chi}_{+\sigma_0})]_{\alpha\alpha'}}{R_{\alpha\alpha'\alpha\alpha'}} \quad (\text{II-53})$$

where a redefined $K(\omega_1, H_1)$ includes all proportionality constants. The integrated intensity (integrated over $\Delta\omega$) from Eq. (II-52) is obtained as:

$$\begin{aligned} g_{\alpha\alpha'}^{\pm} &= \pm K(\omega_1, H_1) \sum_i (I_{\pm}(i))_{\alpha\alpha'} [I_{\pm}(i), (\text{Re } \tilde{\chi}_{+\sigma_0})]_{\alpha\alpha'} \\ &= S_{\alpha\alpha'}^{\pm, p} \times (\text{linewidth})_{\alpha\alpha'}. \end{aligned} \quad (\text{II-54})$$

Equation (II-54) is correct even if the second term in the numerator of Eq. (II-52) involving $\text{Im}(\tilde{\chi})$ is not neglected, since the corresponding integral vanishes. This term thus superposes an intensity distribution odd with respect to $\Delta\omega$ on the lorentzian, but leaves the integrated intensity unchanged.

The expression for peak-height, Eq. (II-53), contains the relaxation width $R_{\alpha\alpha'\alpha\alpha'}$ in the denominator, but in a high resolution experiment the lineshape is determined by a few other factors, such as the inhomogeneity of the magnetic field which contributes significantly to linewidths. These factors should be considered before making a comparison of the peak-heights with the observed spectra. This point was not explicitly considered in earlier studies of relaxation effects by double resonance [11-14, 16, 18, 24].

IIB MAGNETIC FIELD INHOMOGENEITY

1. Sub-ensemble Treatment of Density-matrix

If the magnetic field is inhomogeneous over the sample volume, the spin hamiltonian is different for different spin-systems in the sample and the treatment of the previous section should then be modified to include this. Abragam [ref. 7, p. 26] suggested a method of handling this problem by constructing sub-ensembles, such that the spin-hamiltonian is the same for the systems in each of them, but varies from one sub-ensemble to another. The number of systems in each sub-ensemble should be large enough to treat the problem statistically, but small enough, at the same time to neglect variations in the spin-hamiltonian within a sub-ensemble. The density-matrix theories given earlier [4-9] and sketched in Sec. IIA here, will then be applicable to each sub-ensemble and a final result can be obtained by appropriate averaging over all the sub-ensembles.

For each sub-ensemble one can then define a density-matrix ρ_j , the equation of motion of which is given by:

$$\frac{d\rho_j}{dt} = -i[\mathcal{H}_j, \rho_j], \quad (\text{II-55})$$

where \mathcal{H}_j is total hamiltonian for the j^{th} sub-ensemble and is ^{the} same for all the spin-systems within it. The time variation of ρ_j is then given by:

$$\rho_j = U_j(t) \rho_j(0) U_j^{-1}(t) \quad (\text{II-56})$$

where $U_j(t)$ satisfies the differential equation (see Eq. II-3):

$$\frac{dU_j(t)}{dt} = i \mathcal{H}_j U_j(t) \quad (\text{II-57})$$

An important point to note here is that if the density-matrix ρ for the entire ensemble is defined by averaging over the density-matrices ρ_j of individual sub-ensembles, the transformation connecting $\rho(t)$ and $\rho(0)$ may not, in general, be unitary, even though that connecting $\rho_j(t)$ and $\rho_j(0)$ for each sub-ensemble is unitary [ref. 7, p.27]. However in the present problem it is not necessary to define an average density matrix and the entire double resonance calculation may be performed for each sub-ensemble by solving the equation of motion of ρ_j , given by Eq. (II-55), using the theory sketched in Sec IIA. The relevant macroscopic quantities, like the time derivatives of magnetization, can also be computed for each sub-ensemble, and a final result may be obtained by averaging these quantities over all the sub-ensembles. If the magnetic field inhomogeneity may be assumed to satisfy the requirements of such a treatment then the signal intensity for the total ensemble is obtained by integrating the intensity obtained for a sub-ensemble given by Eq. (II-52), after multiplying it by the shape function of the inhomogeneity.

Assuming that the shape function (normalized) for magnetic field inhomogeneity $h(\Delta\omega)$ is a lorentzian, given by:

$$h(\Delta\omega) = \frac{1/\pi T_2^*}{(\Delta\omega)^2 + (1/T_2^*)^2}, \quad (\text{II-58})$$

where $1/T_2^* = \gamma\Delta H_0$, is the half-width at half-intensity due to field inhomogeneity, multiplying it with Eq. (II-52) and integrating over $\Delta\omega$ from $-\infty$ to $+\infty$, leads to a folding of two lorentzians, which gives another lorentzian having a half-width equal to the sum of half-widths of each component [ref. 7, p. 50].

In addition to the relaxation width and the inhomogeneity width, there is an extra linewidth arising from the experimental set up, due to factors like minute instabilities in the audio-oscillators [23]. This width, though small, is an unavoidable factor, which may be assumed to be the same for all the transitions and may be added to the linewidth, in the expression for intensity, in an ad hoc manner. The peak-height of a non-overlapping transition in a double resonance spectrum is then obtained as:

$$S_{\alpha\alpha'}^{\pm, p} = \pm \frac{K(\omega_1, H_1) \sum_i \gamma_i^2 (I_{\pm}(i))_{\alpha\alpha'} [I_{\pm}(i), (\text{Re} \tilde{\chi} + \sigma_0)]_{\alpha\alpha'}}{\Delta\omega_{\alpha\alpha'}} \quad (\text{II-59})$$

where $\Delta\omega_{\alpha\alpha'}$ is the total half-width of the $\alpha \rightarrow \alpha'$ transition given by:

$$\Delta\omega_{\alpha\alpha'} = R_{\alpha\alpha'\alpha\alpha'} + (\Delta\omega_{\alpha\alpha'})_{\text{Inhomogeneity}} + (\Delta\omega)_{\text{Instability}} \quad (\text{II-60})$$

The peak-height in the single resonance spectrum is then given by:

$$S_{\alpha\alpha'}^{\pm, p} \propto \frac{K(\omega_1, H_1) \sum_i \gamma_i^2 (I_{\pm}(i))_{\alpha\alpha'}^2}{\Delta\omega_{\alpha\alpha'}}, \quad (\text{II-61})$$

where a, a', \dots is the basis in which \mathcal{H}_0 is diagonal and $\Delta\omega_{\alpha\alpha'}$ consists of $R_{\alpha\alpha'\alpha\alpha'}$, $(\Delta\omega_{\alpha\alpha'})_{\text{Inhomogeneity}}$, and $(\Delta\omega)_{\text{Instability}}$.

2. Inhomogeneity Contribution to Linewidths

The linewidths in high resolution n.m.r. spectra of weakly relaxing spin systems are primarily determined by inhomogeneity in the magnetic field. For single resonance spectra this leads to the situation that all the transitions have approximately the same observed linewidths inspite of any variation in relaxation widths arising from the nature of the particular relaxation mechanism for the spins in the molecule. For double resonance spectra, however, the contribution of the magnetic field inhomogeneity can be different for different transitions as shown by Freeman and Anderson [23].

This is basically due to the fact that the process of irradiation of one of the nuclei in a molecule, with a monochromatic frequency, causes frequency shifts of either sign in the transitions of other coupled nuclei, the magnitudes of these shifts depending on the "frequency offset" of irradiation. The "frequency offset" depends on the "local field" at the irradiated nucleus due to the inhomogeneity of H_0 , and these local fields at both the observed and the irradiated nuclei are exactly correlated [27]. In an inhomogeneous field the "frequency offset" has a distribution of values giving rise to a spread in the shifts of the line positions, due to irradiation, which may either cancel or augment the effect of inhomogeneity, giving rise to lines which are narrower or broader compared to single resonance *lines*.

(a) Single Resonance:- In general, the width $\Delta\omega_{\alpha\alpha'}$ caused by an inhomogeneous field of width ΔH_0 in a transition $\alpha \rightarrow \alpha'$, may be written as:

$$(\Delta\omega_{\alpha\alpha'})_{\text{Inhomogeneity}} = (\Delta H_0) \left| \sum_i \gamma_i \frac{\partial \omega_{\alpha\alpha'}}{\partial \omega_i} \right|, \quad (\text{II-62})$$

where $\omega_{\alpha\alpha'}$ is the frequency of the $\alpha \rightarrow \alpha'$ transition and ω_i the *l*armor frequencies of various spins in a molecule. For a weakly coupled single resonance spectrum Eq. (II-62) gives $\gamma_i \Delta H_0$. In the case of strongly coupled single resonance spectrum, the *l*armor frequencies of other nuclei ω_j enter the expression for $\omega_{\alpha\alpha'}$ through the chemical

shift $(\omega_i - \omega_j)$ and if all the strongly coupled nuclei belong to the same species, Eq. (II-62) essentially gives $\gamma_i \Delta H_0$ for all the transitions involving nuclei "i" and is thus the same for all of them.

(b) Double Resonance - Weakly Coupled Spin Systems:- For the double resonance case ω_j enters the expression for $\omega_{\alpha\alpha'}$ (Eq. II-62) also through the "frequency offset" A_j of the irradiated nucleus and for a weakly coupled spin system Eq. (II-62) becomes:

$$(\Delta\omega_{\alpha\alpha'})_{\text{Inhomogeneity}} = (\Delta H_0) \left| \left(\gamma_i + \frac{\gamma_j}{2\pi} \frac{\partial \omega_{\alpha\alpha'}}{\partial A_j} \right) \right|. \quad (\text{II-63})$$

Thus the contribution of inhomogeneity to the linewidths of different transitions is different and the fractional change in this contribution (with reference to single resonance) is given by the slope of the curve $\omega_{\alpha\alpha'}/2\pi$ versus A_j . Any transition for which this slope becomes $(-\gamma_i/\gamma_j)$, the inhomogeneity contribution becomes zero and the only width that remains is due to relaxation and instability. This situation has an interesting similarity with spin echoes in which the fanning out of the spins due to inhomogeneity of the magnetic field is completely recovered. This also suggests the possibility that by double resonance the contribution of inhomogeneity to the linewidths in high resolution n.m.r. can be estimated and, therefore, an estimate of relaxation widths may be obtained. A quantitative consideration of this effect leads to an

accurate estimate of the relaxation parameters by double resonance.

(c) Estimate by Double Resonance:- For any two transitions $\alpha \rightarrow \alpha'$ and $\beta \rightarrow \beta'$ in the double resonance spectrum of a weakly coupled spin system the difference in the linewidths, from Eqs. (II-63) and (II-60), is given by:

$$(\Delta\omega)_{\alpha\alpha'} - (\Delta\omega)_{\beta\beta'} = (R_{\alpha\alpha'\alpha\alpha'} - R_{\beta\beta'\beta\beta'}) + (\gamma_i \Delta H_0) \times \left| \left(\left| \frac{\gamma_i}{\gamma_j} + \frac{1}{2\pi} \frac{\partial \omega_{\alpha\alpha'}}{\partial A_j} \right| - \left| \frac{\gamma_i}{\gamma_j} + \frac{1}{2\pi} \frac{\partial \omega_{\beta\beta'}}{\partial A_j} \right| \right) \right|. \quad (\text{II-64})$$

ΔH_0 may be readily estimated from this equation by choosing two transitions $\alpha \rightarrow \alpha'$ and $\beta \rightarrow \beta'$ having widely different slopes provided the relaxation widths are small compared to inhomogeneity contributions or that the two transitions $\alpha \rightarrow \alpha'$ and $\beta \rightarrow \beta'$ have nearly equal relaxation widths, in which case the first term in Eq. (II-64) will be small compared to the second, and may be neglected. The most convenient method is to look for, in the double resonance spectra, transitions having slopes opposite in sign and magnitudes close to unity. Normally in double resonance spectra transitions with slopes opposite in sign are present. As shown below, in weakly coupled spin systems, there are always pairs of transitions whose slopes are equal in magnitude and opposite in sign.

Consider a weakly coupled spin system of the type $A_n X_m$. The diagonalized hamiltonian in the rotating frame

$\mathcal{H}_0^R(D)$ for irradiation of X spins can be written as [28]:

$$\mathcal{H}_0^R(D) = 2\pi \left\{ A_A I_Z(A) + [(A_X + J I_Z(A))^2 + v_{2X}^2]^{\frac{1}{2}} I_Z(X) \right\}, \quad (\text{II-65})$$

where $I_Z(A) = \sum_{i=1}^n I_Z(i)$ and $I_Z(X) = \sum_{j=1}^m I_Z(j)$, in which i and j are respectively A and X types of spins. J is the spin-spin coupling constant between the A and the X nuclei. Transitions belonging to A spins are those between states $|m(i), m(j)\rangle \rightarrow |m(i) \pm 1, m(j)\rangle$. Consider a pair of A transitions between the states $|m(i), m(j)\rangle \rightarrow |m(i)-1, m(j)\rangle$ and $|m(i), -m(j)\rangle \rightarrow |m(i)-1, -m(j)\rangle$. Their transition frequencies are respectively given by:

$$\begin{aligned} \omega_{\alpha\alpha'} = 2\pi \left\{ A_A + [(A_X + J m(i))^2 + v_{2X}^2]^{\frac{1}{2}} m(j) \right. \\ \left. - [(A_X + J (m(i)-1))^2 + v_{2X}^2]^{\frac{1}{2}} m(j) \right\} \end{aligned} \quad (\text{II-66})$$

and

$$\begin{aligned} \omega_{\beta\beta'} = 2\pi \left\{ A_A - [(A_X + J m(i))^2 + v_{2X}^2]^{\frac{1}{2}} m(j) + \right. \\ \left. + [(A_X + J ((m(i)-1)))^2 + v_{2X}^2]^{\frac{1}{2}} m(j) \right\}. \end{aligned} \quad (\text{II-67})$$

The slopes of these transitions are given by:

$$\frac{1}{2\pi} \frac{\partial \omega_{\alpha\alpha'}}{\partial A_X} = \frac{(A_X + J m(i)) m(j)}{[(A_X + J m(i))^2 + v_{2X}^2]^{\frac{1}{2}}} - \frac{[A_X + J (m(i)-1)] m(j)}{[\{A_X + J (m(i)-1)\}^2 + v_{2X}^2]^{\frac{1}{2}}} \quad (\text{II-68})$$

and

$$\frac{1}{2\pi} \frac{\partial \omega_{\beta\beta'}}{\partial A_X} = - \frac{1}{2\pi} \frac{\partial \omega_{\alpha\alpha'}}{\partial A_X} \quad (\text{II-69})$$

and are equal in magnitude and opposite in sign. It is then possible to estimate the inhomogeneity contribution to the linewidths from the values of these slopes and the observed difference in linewidths.

IIC SOLUTIONS FOR $\tilde{\chi}$

1. "High" Amplitude of Irradiation; Bloch Approximation

Bloch proposed [4] that if, in the rotating frame in a representation in which the stationary part of the spin hamiltonian is diagonal, the difference between any two energy levels is large compared to the corresponding relaxation matrix elements such that :

$$|E_{\alpha} - E_{\alpha'}| \gg |\Gamma_{\alpha\alpha'}| \quad (\text{II-70})$$

for each $\alpha \neq \alpha'$, then the off-diagonal matrix elements of the stationary part of the spin density-matrix ($\tilde{\chi} + \sigma_0$) are negligible in that representation. This condition (II-70) was shown to obtain even when the irradiation frequency coincided with a single resonance transition [9], provided

$$|\gamma H_2| \gg |\Gamma_{\alpha\alpha'}|. \quad (\text{II-71})$$

Irradiation strengths termed as "high" in this study refer to amplitudes of irradiation which satisfy the condition (II-71).

Under the approximation that $(\tilde{\chi} + \sigma_0)$ is diagonal in the $\alpha, \alpha' \dots$ basis, (known as Bloch approximation), the diagonal elements of $\tilde{\chi}$ are given by (from Eq. (II-42)):

$$\sum_{\beta} R_{\alpha\alpha\beta\beta} \tilde{\chi}_{\beta\beta} = 2 \sum_{\beta < \beta'} R_{\alpha\alpha\beta\beta'} (\sigma_0)_{\beta\beta'} \quad (\text{II-72})$$

and the off-diagonal elements of $\tilde{\chi}$ equal those of $(-\sigma_0)$. The solution for $\tilde{\chi}$ obtained from Eq. (II-72) depends only on the relative values of various relaxation matrix elements and not on their absolute values. Thus the double resonance spectra for which the condition (II-71) is satisfied, give information only about the relative values of relaxation matrix elements.

2. "Low" Amplitudes of Irradiation

If the amplitude of irradiation does not satisfy the condition (II-71), the entire set of Eqs. (II-40) to (II-42) need be solved, in general. These solutions then depend on the absolute values of the relaxation matrix elements. Two special cases may further be considered. If the strength of irradiation is smaller than the linewidths in the single resonance spectrum, only intensity changes and no splittings are observed in the double resonance spectrum (generalised Overhauser effect)[4]. The strength of irradiation is termed as "low" for such cases and it is convenient to obtain a steady-state solution for $\chi(t)$ in the laboratory frame rather than in the rotating frame.

Secondly, if in the double resonance spectrum line splittings are observed and the amplitude of irradiation is not high enough to satisfy the inequality (II-71) [this is an intermediate range of strength of irradiation when $|\gamma H_2| \sim$ observed linewidths], it is possible to obtain a solution for $\tilde{\chi}$, in the rotating *frame*, without solving the complete set of Eqs. (II-41) and (II-42) by making what may be called a partial Bloch approximation [9]. These two methods of solution will be discussed briefly in the following.

(a) Laboratory Coordinate Solution:- The solution for $\chi(t)$ is obtained by assuming that the diagonal elements of χ are independent of time and that the off-diagonal elements vary as:

$$\chi(t)_{ab} = Z_{ab}^+ e^{i\omega_2 t} + Z_{ab}^- e^{-i\omega_2 t}, \quad (a \neq b) \quad (\text{II-73})$$

where a, b is the basis in which \mathcal{H}_0 is diagonal. The equation of motion of the spin density matrix to be solved for this case is given by Eq. (II-14). If in the single resonance spectrum there are no overlapping transitions present (line separations \gg linewidths) (simple line approximation [ref. 7, p. 522, 15]), it can be assumed that the irradiation with "low" amplitudes, induces only one off-diagonal matrix element of χ , between the pair of states affected by the irradiation. If the frequency

of irradiation coincides with a single resonance transition $a \rightarrow b$, one obtains, putting $\eta(t) = 0$ in Eq. (II-14), for the matrix elements of $\chi(t)$ the following equations [ref. 7, p. 522, 15]:

$$\sum_{b' \neq a} R_{aab'b'} (\chi_a - \chi_{b'}) = 2I, \quad (\text{II-74A})$$

$$\sum_{a' \neq b} R_{bba'a'} (\chi_b - \chi_{a'}) = -2I, \quad (\text{II-74B})$$

$$\sum_{\substack{d \neq c \\ c \neq a, b}} R_{ccdd} (\chi_c - \chi_d) = 0, \quad (\text{II-74C})$$

and

$$\sum_a \chi_a = 0, \quad (\text{II-75})$$

where $I = \text{Im} (zd^*)$, $\chi_a = \langle a | \chi | a \rangle$, $d = \langle b | D_{2+} | a \rangle = \langle a | D_{2-} | b \rangle^*$ and $z = \langle b | z^+ | a \rangle = \langle a | z^- | b \rangle^*$. Equations (II-74) and (II-75) constitute $(N+1)$ homogeneous linear simultaneous equations in N unknowns (χ_a) and have a unique solution which can be represented as $\chi_a = T_a I$, where T_a are functions of $R_{a'a'b'b'}$ type of elements and are independent of the strength of the irradiating r.f. field. The off-diagonal matrix element of χ and the strength of irradiation are included in I . A solution for χ leads to, for any transition $a' \rightarrow b'$;

$$\chi_{a'} - \chi_{b'} = \frac{q |d^2| \omega_0 T_{a'b'} T_2}{1 + |d^2| T_2 T_{ab}}, \quad (\text{II-76})$$

where $T_{a'b'} = T_{a'} - T_{b'}$, $T_2 = -1/R_{abab}$ and $q = \hbar/NkT$.

The expression for the intensity of any transition $a' \rightarrow b'$ can be obtained in a manner similar to that outlined in Sec. IIA, by assuming that the diagonal elements of $\eta(t)$ are zero and that the off-diagonal elements vary as $\exp(\pm i\omega_{\pm}t)$. The expression for integrated intensity is then obtained as:

$$J_{a'b'}^{\pm} \propto (I_{\pm})_{a'b'}^2 [(\chi + \sigma_0)_{b'b'} - (\chi + \sigma_0)_{a'a'}] \quad (\text{II-77})$$

from which the peak height can be obtained by dividing by the total width of the line.

For the purpose of the analysis of double resonance spectra it is useful to compute the ratio $[S/(S^0 - S)]_{a'b'}$ where S^0 and S are respectively the single and double resonance integrated intensities of the transition $a' \rightarrow b'$. This ratio is given by:

$$\begin{aligned} \left(\frac{S}{S^0 - S} \right)_{a'b'} &= \frac{[(\sigma_0)_{b'b'} - (\sigma_0)_{a'a'} + \chi_{b'} - \chi_{a'}] \cdot q \omega_0 - (\chi_{a'} - \chi_{b'})}{\chi_{a'} - \chi_{b'}} = \frac{q \omega_0 - (\chi_{a'} - \chi_{b'})}{(\chi_{a'} - \chi_{b'})} \\ &= \frac{1}{T_{a'b'} T_2} \frac{1}{|d^2|} + \frac{T_{ab} - T_{a'b'}}{T_{a'b'}}. \end{aligned} \quad (\text{II-78})$$

Equation (II-78) gives a straight line when the ratio $[S/(S^0-S)]_{a'b'}$ is plotted against $1/|d^2|$, having a intercept which depends only on the relative values of various relaxation matrix elements and a slope which depends on the absolute values. Kuhlmann and Baldeschwieler [15] studied the behaviour of this ratio for a range of values of $|d^2|$, chosen such that line splittings are not observed in the double resonance spectra.

For the above plot the absolute change in intensity of a transition between two different spectra (single and double resonance) is needed. This presents experimental difficulties unless there is a reference line in the spectrum which is not perturbed by irradiation. To avoid this, a comparison between the ratios of any two transitions $a' \rightarrow b'$ and $c' \rightarrow d'$ may be obtained, both in single and double resonance spectra. If R represents the ratio of the double resonance intensities of any two transitions $a' \rightarrow b'$ and $c' \rightarrow d'$ divided by the ratio of their intensities in single resonance:

$$R = (S_{a'b'}/S_{c'd'})/(S_{a'b'}^0/S_{c'd'}^0) , \quad (\text{II-79})$$

then

$$\frac{R+1}{R-1} = \frac{2}{T_2(T_{a'b'} - T_{c'd'})} \frac{1}{|d^2|} + \frac{[-2T_{ab} + T_{a'b'} - T_{c'd'}]}{[T_{a'b'} - T_{c'd'}]} , \quad (\text{II-80})$$

This equation again gives a straight line having ~~an~~ intercept $(-2T_{ab} + T_{a'b'} - T_{c'd'})/(T_{a'b'} - T_{c'd'})$ which depends only on the relative values of various relaxation matrix elements and a slope $2/T_2(T_{ab} - T_{cd})$ which depends on the absolute values.

If there are overlapping transitions present in the single resonance spectrum more than one off-diagonal elements of χ can become simultaneously significant and the procedure becomes involved (see Kuhlmann and Baldeschwieler [15]).

(b) Partial Bloch Approximation:- If splittings are obtained in the double resonance spectrum, the rotating coordinate analysis has to be used. However, if the strength of irradiation is not large enough to satisfy the inequality (II-71) for all transitions, Eq. (II-70) will still be true for all pairs of states other than the two connected by irradiation, if the other transitions have a separation, from the irradiated one, large compared to ν_2 . In such cases an approximation that $(\tilde{\chi} + \sigma_0)$ has off-diagonal elements only between those two states can be made [9], and instead of solving all the N^2 equations (II-40) to (II-42), a solution for $\tilde{\chi}$ can be obtained by solving only $(N+2)$ equation (N equations from Eq. (II-42) and one from each Eqs. (II-40 and II-41)). The solutions for $\tilde{\chi}$ will, in this case, be dependent on the absolute values of relaxation matrix elements. In the limit of no splittings this solution reduces to the laboratory frame solution.

Chapter III

RELAXATION MECHANISMS AND CORRELATIONS

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III - RELAXATION MECHANISMS AND CORRELATIONS

IIIA INTERACTION HAMILTONIANS AND CORRELATION CONSTANTS

The hamiltonians for various interactions which can contribute to relaxation of spin $\frac{1}{2}$ nuclei in liquid samples and expressions for correlation constants are given in this section. A general expression for the relaxation hamiltonian considered as a random function of time, has already been given in Eq. (II-11) and some properties of spin operators $A^{(q)}$ and lattice functions $F^{(q)}$ in Eqs. (II-12) and (II-13).

1. External Isotropic Random Fields

This mechanism generally includes various intermolecular and intramolecular interactions for which explicit calculations are not feasible and a combined effect of all such interactions is treated as an isotropic random field at the sites of the spins of interest [29]. The sources for these fields are external to the spin system of interest but not necessarily external to the molecule. The interaction of these fields with a spin 'i' can be expressed as [ref. 7, p. 508]:

$$\mathcal{H}'(t) = - \sum_i \gamma_i \underline{I}(i) \cdot \underline{H}_i(t) , \quad (\text{III-1})$$

such that the spin operators and lattice functions as defined in Eq. (II-11) can be expressed as:

$$A_i^{(+1)} = \frac{1}{\sqrt{2}} I^{\pm}(i) ; \quad A_i^{(0)} = I^Z(i) \quad (\text{III-2})$$

and

$$F_i^{(+1)}(t) = \pm \frac{\gamma_i}{\sqrt{2}} (H_i^x(t) \pm i H_i^y(t)) ; F_i^{(0)}(t) = -\gamma_i H_i^z(t) .$$

(III-3)

These random fields are considered isotropic, which is introduced through the relation [ref. 7, p. 508, 9]:

$$\begin{aligned} \langle |F_i^{(q)}(t)|^2 \rangle_{av} &= \gamma_i^2 \langle |H_i^z(t)|^2 \rangle_{av} = \frac{\gamma_i^2}{2} \langle |H_i^+(t)|^2 \rangle_{av} \\ &= \frac{\gamma_i^2}{2} \langle |H_i^-(t)|^2 \rangle_{av} = f(i) , \end{aligned} \quad \text{(III-4)}$$

where $f(i)$ is the mean square field at the site of spin "i".

The degree of correlation between random fields at the sites of different spins in a molecule may be defined as:

$$C_{ii'} = \frac{\langle F_i^{(q)}(t) F_{i'}^{(q)}(t) \rangle_{av}}{[\langle |F_i^{(q)}(t)|^2 \rangle_{av} \langle |F_{i'}^{(q)}(t)|^2 \rangle_{av}]^{\frac{1}{2}}} ,$$

(III-5)

where $C_{ii'}$ is the correlation constant between nuclei i and i' and varies between 0 and 1 for the limiting cases of no correlation and complete correlation between the fields respectively. This definition of $C_{ii'}$ is chosen here such that the mean square values of the random fields $\langle |F_i^{(q)}(t)|^2 \rangle_{av}$ and $\langle |F_{i'}^{(q)}(t)|^2 \rangle_{av}$ need not be equal for partially or completely correlated cases as has been

considered by earlier workers [ref. 7, p. 503, 11,14-16].

Extreme-narrowing assumption is generally used for calculations with this mechanism, but depends upon the specific interaction being considered as a random field.

2. Internal Dipole-Dipole Interaction

The interaction hamiltonian for direct dipole-dipole coupling between different spins can be written as [ref. 7, p. 289, 15, 30]

$$\mathcal{H}' = \sum_N \sum_{q=-2}^{+2} (-1)^q A_N^{(q)} F_N^{(-q)}(t) \quad (\text{III-6})$$

such that

$$A_N^{(+2)} = I_N^+ S_N^+ ; \quad A_N^{(\pm 1)} = \mp (I_N^+ S_N^z + I_N^z S_N^+),$$

$$A_N^{(0)} = \left(\frac{8}{3}\right)^{\frac{1}{2}} \left[I_N^z S_N^z - \frac{1}{4} (I_N^+ S_N^- + I_N^- S_N^+) \right] \quad (\text{III-7})$$

and

$$F_N^{(q)} = -\left(\frac{6\pi}{5}\right)^{\frac{1}{2}} \hbar \gamma_{I_N} \gamma_{S_N} r_N^{-3} Y_2^q(\theta_N, \varphi_N) , \quad (\text{III-8})$$

where the subscript N refers to a pair of spins I_N and S_N , r_N is the distance between them, and Y_2^q are the spherical harmonics of rank 2, with θ_N and φ_N specifying the orientation of \underline{r}_N relative to the laboratory-fixed coordinate system. Transforming F_N^q 's to a molecule fixed coordinate system, the correlation constants between any two pairs N

and N' can be obtained by averaging over all the molecular orientations, as [15,30]:

$$\begin{aligned} g_{NN'} &= \sum_q \left\langle F_I^{(q)}(t)^* F_{N'}^{(q)}(t) \right\rangle_{av} \\ &= \frac{3}{20} \hbar^2 \gamma_{I_N} \gamma_{S_N} \gamma_{I_{N'}} \gamma_{S_{N'}} r_N^{-3} r_{N'}^{-3} (3 \cos^2 \psi_{NN'} - 1), \end{aligned} \quad (\text{III-9})$$

where $\psi_{NN'}$ is the angle between \underline{r}_N and $\underline{r}_{N'}$. Equation (III-9) is obtained by using ^{the} addition theorem of spherical harmonics. For $N = N'$, $\psi_{NN} = 0$ and g_{NN} are known as auto-correlation constants and for $N \neq N'$, $g_{NN'}$ are called cross-correlation constants which can be calculated from the geometry of the molecule.

3. Scalar Coupling

The scalar coupling between a spin $I = \frac{1}{2}$ nucleus and a spin $S \gg 1$ nucleus acts as a relaxation mechanism for spin I , if the spin states of \underline{S} are having rapid time dependence due to e.g. its fast quadrupole relaxation rate. The relaxation hamiltonian for scalar coupling can be expressed as [ref. 7, p. 310]:

$$\mathcal{H}'(t) = 2\pi \sum_i J_{is} \underline{I}(i) \cdot \underline{S}(t). \quad (\text{III-10})$$

In this the spin \underline{S} is treated as part of the lattice. The sum over 'i' is over all the spins \underline{I} . The spin operators

are expressed as in Eq. (III-2) and the lattice operators can be expressed as (see Eq. II-11):

$$F^{(+1)}(t) = \frac{1}{\sqrt{2}} S^+(t) ; \quad F^{(0)}(t) = S^z(t) . \quad (\text{III-11})$$

There is a complete correlation between the interactions of various spins $\underline{I}(i)$ with the same spin $\underline{S}(t)$ in a molecule and it may be assumed that there is no correlation of these interactions with that to another spin $\underline{S}'(t)$ in the molecule.

4. Spin-Rotation Interaction

The interaction of the nuclear magnetic moment with the magnetic field produced at its site by the rotation of the molecule containing the nucleus is known as spin-rotation interaction and can cause nuclear magnetic relaxation. The hamiltonian for the spin rotation interaction is given by [31],

$$\mathcal{H}(t) = \underline{I} \cdot \underline{C}(t) \cdot \underline{J} , \quad (\text{III-12})$$

where \underline{J} is the angular momentum of the molecule containing the spin \underline{I} and \underline{C} is the spin-rotation tensor. Assuming a spherical model of the molecule containing nucleus I , one obtains in the molecule fixed frame $C_z = C_{||}$ and $C_x = C_y = C_{\perp}$ and the interaction hamiltonian[†] in the

[†] A general expression for asymmetric rotor is given by Huntress [32].

molecule fixed frame as [31]:

$$[\mathcal{H}(t)]^{(i)} = \sum_{q'=-1}^{+1} C_{q'} (A^{(q')})^{(i)} (J^{(-q')})^{(i)}, \quad (\text{III-13})$$

where the superscript (i) indicates molecule fixed frame values, and

$$A^{(0)} = I^Z; \quad A^{(\pm 1)} = \mp \frac{1}{\sqrt{2}} I^{\pm}, \quad (\text{III-14})$$

$$J^{(0)} = J^Z; \quad J^{(\pm 1)} = \mp \frac{1}{\sqrt{2}} (J^X \pm i J^Y), \quad (\text{III-15})$$

and

$$C_0 = C_{II}; \quad C_{\pm 1} = -C_I. \quad (\text{III-16})$$

Transforming A and J from molecule fixed frame to *the* laboratory coordinate by using the relation:

$$(A^{(q')})^{(i)} = \sum_q A^{(q)} D_{qq'}^{(1)}(\Omega), \quad (\text{III-17})$$

and a similar relation for J , *the* interaction hamiltonian in the laboratory frame is given by [31]:

$$\mathcal{H}(t) = \sum_q (-1)^q A^{(q)} F^{(-q)}, \quad (\text{III-18})$$

where

$$F^{(-q)} = (-1)^q \sum_{q', q''} C_{q'} D_{q'q}^{(1)*}(\Omega) D_{-q, q''}^{(1)}(\Omega) J^{(q'')}. \quad (\text{III-19})$$

The spin-rotation interaction is completely correlated for various spins in the same molecule and completely uncorrelated for spins in different molecules [31].

The spin-rotation constant C is usually smaller for protons compared to nuclei like F^{19} and is usually not an efficient relaxation mechanism for protons [33,34].

5. Anisotropic Chemical Shift

Under the influence of an external magnetic field H the induced precession of the electrons causes an interaction of the type $-\gamma \underline{I} \cdot \underline{A} \cdot \underline{H}$, where \underline{A} is the chemical shielding tensor of rank 2 [ref. 7, p. 315]. The trace of this tensor gives rise to the chemical shift and the anisotropic part A' of this tensor is time dependent in liquids because of molecular tumbling and causes relaxation in nuclear magnetic resonance. The interaction hamiltonian is given in ref. 7, p. 315.

No examples are known in which this interaction makes significant contribution to proton relaxation, presumably because of the small chemical shifts of protons.

IIIB CONDITIONS UNDER WHICH VARIOUS INTERACTIONS CAN BE APPROXIMATED BY A RANDOM FIELD

The random field mechanism is often convenient to use, for ^{the} description of relaxation effects, in cases like the analysis of double resonance spectra. This mechanism is linear in its spin variables and possesses isotropy,

resulting in a considerable simplification in the calculation of a large number of relaxation matrix elements involved in the analyses. This mechanism, serves as a model for describing the effects of a complex set of intermolecular and intramolecular interactions often present in a complicated spin system. A knowledge of the values of the random fields at the sites of various spins in a molecule and the correlations between these fields could then be used to indicate the various interactions responsible for these fields. It, therefore, becomes important to examine the conditions under which various interactions can be approximated by a model of external isotropic random fields.

1. General Properties of Random Fields

The hamiltonian for external random fields and the properties of their spin and lattice operators, including isotropy (Eq. III-4) and the secular approximation (Eq. II-13) have been given earlier. The processes responsible for time dependence in the random field hamiltonian will be assumed to be Markoffian, leading to a correlation function $G(\tau)$ as [ref. 7, p. 297]:

$$G(\tau) = \left\langle F^{(q)*}(t) F^{(q)}(t-\tau) \right\rangle_{av} = \left\langle |F^{(q)}(t)|^2 \right\rangle_{av} e^{-|\tau|/\tau_c}, \quad (\text{III-20})$$

where τ_c is the correlation time and is the characteristic time for molecular reorientation, which is responsible for time dependence of $\mathcal{H}(t)$.

Substituting the form of $\mathcal{H}(t)$ from Eq. (II-11), for a single spin, into the expression for spectral density of the "non-viscous liquid" approximation Eq. (II-34), and using Eqs. (III-2) - (III-4) and the relations:

$$e^{-i \mathcal{H}_0 \tau} I^q e^{i \mathcal{H}_0 \tau} = I^q e^{-i \omega_I^q \tau}, \quad (\text{III-21})$$

where $\omega_I = -\gamma_I H_0$, $I^{\pm 1} = I^{\pm}$ and $I^0 = I^z$, gives:

$$\begin{aligned} J_{\alpha\beta\alpha'\beta'}^{\text{nv}} &= \sum_{q=-1}^{+1} \frac{2\tau_c}{[1+(\omega_I^q \tau_c)^2]} \langle \alpha | A^{(q)} | \beta \rangle \langle \beta' | A^{(-q)} | \alpha' \rangle \\ &\quad (-1)^q \langle |F^{(q)}(t)|^2 \rangle_{\text{av}} \\ &= f \sum_{q=-1}^{+1} \frac{2\tau_c}{[1+(\omega_I^q \tau_c)^2]} \frac{1}{(|q|+1)} \langle \alpha | I^q | \beta \rangle \langle \beta' | I^{-q} | \alpha' \rangle. \end{aligned} \quad (\text{III-22})$$

In the "extreme narrowing" case when $\omega_I \tau_c \ll 1$, (see Eq. II-35):

$$\begin{aligned} J_{\alpha\beta\alpha'\beta'}^{\text{en}} &= 2f\tau_c \sum_{q=-1}^{+1} \frac{1}{(|q|+1)} \langle \alpha | I^q | \beta \rangle \langle \beta' | I^{-q} | \alpha' \rangle \\ &= 2f\tau_c \left[\frac{1}{2} (I^+)_{\alpha\beta} (I^-)_{\beta'\alpha'} + (I^z)_{\alpha\beta} (I^z)_{\beta'\alpha'} \right. \\ &\quad \left. + \frac{1}{2} (I^-)_{\alpha\beta} (I^+)_{\beta'\alpha'} \right]. \end{aligned} \quad (\text{III-23})$$

Equations (III-22) and (III-23) for the spectral densities contain the essential features of this mechanism. The expressions for T_1 and T_2 can simply be obtained from these equations by calculating the values for a single spin $\frac{1}{2}$ case and noting that $1/T_1 = 2 J_{1212}$ and $1/T_2 = -2 J_{1122} + J_{1212}$, where $I^Z|1\rangle = \frac{1}{2}|1\rangle$ and $I^Z|2\rangle = -\frac{1}{2}|2\rangle$.

2. Various Interactions

The procedure for obtaining the conditions under which various interactions can be approximated by an isotropic random field will be to obtain the spectral densities under 'non-viscous liquid' and 'extreme-narrowing' approximations and compare them with Eqs. (III-22 and 23). All the interactions mentioned in Sec. IIIA will be considered except anisotropic chemical shift, which obviously cannot be approximated by an isotropic field.

(a) Dipole-Dipole Interaction:- This is a direct magnetic interaction between two spins and depends both on the distance between the spins and the orientation of internuclear vector with respect to a space fixed frame. The two spins may either belong to the same molecule((i) intramolecular dipole-dipole interaction) or different molecules((ii) intermolecular dipole-dipole interaction). The time dependence in these dipolar interactions are due to molecular rotation in (i) and due to both translation and rotation in (ii). We will consider both these interactions separately.

(i) Intramolecular dipole-dipole interaction;- If both the spins of interest are spin $\frac{1}{2}$ nuclei then this interaction is generally treated explicitly in relaxation calculations through what are known as internal dipole-dipole interactions, the expressions for which have been given in Sec. IIIA, and these interactions cannot be approximated as random fields. However, if one of the spins has rapid time dependence in its spins states arising from a fast quadrupole relaxation rate (spin ≥ 1) then this interaction, as shown below, can be approximated as an external random field.

The dipole-dipole interaction hamiltonian Eq.(III-6-8) can be rewritten for a single pair as,

$$\begin{aligned} \mathcal{H}'(t) &= I^+ [S^+ F^{(-2)} + S^z F^{(-1)} - \frac{1}{4} \sqrt{\frac{8}{3}} S^- F^{(0)}] + I^z [S^+ F^{(-1)} \\ &+ \sqrt{\frac{8}{3}} S^z F^{(0)} - S^- F^{(+1)}] + I^- [-\frac{1}{4} \sqrt{\frac{8}{3}} S^+ F^{(0)} - S^z F^{(+1)} + S^- F^{(+2)}] \\ &= \sum_{q=-1}^{+1} I^q \sum_{p=-1}^{+1} c_p^q S^p F^{-(p+q)} \quad , \end{aligned} \quad \text{(III-24)}$$

where

$$\begin{aligned} c_{+1}^{+1} &= c_{-1}^{-1} = c_0^{+1} = c_{+1}^0 = c_0^{-1} = -c_{-1}^0 = 1 \\ c_{-1}^{+1} &= c_{+1}^{-1} = -\frac{1}{4} \sqrt{\frac{8}{3}} ; \quad c_0^0 = \sqrt{\frac{8}{3}} \quad . \end{aligned} \quad \text{(III-24A)}$$

Substituting this hamiltonian in the expression for spectral densities (Eq. II-34) for "non-viscous liquid" approximation and making use of the relations (III-21) and similar relations for \tilde{S} , one gets:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = \int_{-\infty}^{+\infty} d\tau \sum_{\substack{q, q' \\ p, p'}} \langle \alpha | I^q C_p^q S^p | \beta \rangle \langle \beta' | I^{-q'} C_{-p}^{-q'} S^{-p'} | \alpha' \rangle \\ e^{i(\omega_I q' + \omega_S p')\tau} \left\langle F^{-(p+q)}(t) F^{-(p'+q')}^*(t-\tau) \right\rangle_{av} \quad (\text{III-25})$$

Consider now the case when one of the spins, say spin \underline{S} , has a rapid time dependence arising from interactions which do not involve \underline{I} . This can arise from rapid quadrupolar relaxation of spin \underline{S} , if $S \geq 1$. The motion of spin \underline{S} may then be assumed to be unaffected by its interaction with spin \underline{I} and the rapid relaxation of \underline{S} may be assumed to be described by Bloch equations. This condition is usually obtained for $S = 1$ and for $S > 1$ if "extreme narrowing" is valid for molecular motions responsible for relaxation of \underline{S} [3]. This latter condition also leads to $\tau_1 = \tau_2$, the characteristic times in Bloch equations. In addition if τ_1 and τ_2 are very much different from τ_c , the correlation time for molecular rotation, it is permissible to separately average the F_S^+ and F_S^- in Eq. (III-25) giving for $S[7]$:

$$\left\langle S_z(0) S_z(\tau) \right\rangle_{av} = \frac{S(S+1)}{3} e^{-\tau/\tau_1} \\ \left\langle S_{\pm}(0) S_{\mp}(\tau) \right\rangle_{av} = \frac{2S(S+1)}{3} e^{-\tau/\tau_2} e^{\pm i\omega_S \tau} \quad (\text{III-26})$$

Equation (III-25) will now have a correlation constant given by:

$$\frac{1}{\tau'_c} = \frac{1}{\tau_c} + \frac{1}{\tau(|p|+1)} \quad . \quad (\text{III-27})$$

In the limit $\tau_c \ll \tau(|p|+1)$, true for most of the cases, $\tau'_c \cong \tau_c$. Making use of this and of Eqs. (III-20,26,27) and (II-13), and substituting the value of C_p^q from Eq. (III-24A) in Eq. (III-25) one obtains for spectral densities:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = \frac{2S(S+1)}{3} \frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r^6} \sum_q \left[\frac{2\tau_c}{1+(\omega_{Iq}\tau_c)^2} \right] \frac{1}{(|q|+1)} \\ \times \langle \alpha | I^q | \beta \rangle \langle \beta' | I^{-q} | \alpha' \rangle \quad (\text{III-28})$$

which is identical to the expression (III-22) with

$$f = \frac{2S(S+1)}{3} \left(\frac{\gamma_I^2 \gamma_S^2 \hbar^2}{r^6} \right) \quad . \quad (\text{III-29})$$

Thus the conditions for intramolecular dipole-dipole interaction to be approximated as random field are that, the time dependences of spin \underline{S} and that of F are widely different and that Bloch equations can be assumed for motion of spin \underline{S} .

Correlations:- If there are two or more spins $\underline{I}(i)$ in the molecule having dipolar interaction with a spin \underline{S} , then the correlation $C_{ii'}$ between the random fields produced by the \underline{S} spin at the different spins $\underline{I}(i)$ are given by, using Eq. (III-9) and Eq. (III-5),

$$C_{ii'} = \frac{1}{2} (3 \cos^2 \psi_{ii'} - 1), \quad (\text{III-30})$$

where $\psi_{ii'}$ is the angle between the vectors joining i and i' spins with the spin S . In such a case it is then possible that the random fields may be completely correlated (if the three spins lie in a straight line) having different mean square fields. The correlation with more than one spin having fast time dependence will also be given by Eq. (III-30), since $\tau_c \ll \tau(|p|+1)$.

(ii) Intermolecular dipole-dipole interaction;- In this case both rotational and translational motion of the molecule are responsible for changes in orientation and magnitude of internuclear axis. However, assuming in the following that the molecules are spherical and that the spins of interest are at centers of the molecules (in which case the rotational motion will not be effective), expressions for spectral densities will be obtained. The case in which the spin is not at the center of the spherical molecule does not alter the arguments of this section, and will be briefly discussed.

The interaction hamiltonian can be expressed as (see Eq. III-24):

$$\mathcal{H}'(t) = \sum_j \sum_q I^q \sum_p C_p^q S_j^p F_j^{-(p+q)}(t), \quad (\text{III-31})$$

where the sum is over all j nuclei external to the molecule. The spectral densities Eq. (III-25) in this case will then become:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = \sum_j \int_{-\infty}^{+\infty} d\tau \sum_{\substack{q, q' \\ p, p'}} \left\langle \left\langle \alpha \left| I^q C_p^q S_j^p \right| \beta \right\rangle \left\langle \beta' \left| I^{-q'} C_{-p}^{-q'} S_j^{-p'} \right| \alpha' \right\rangle \right. \\ \left. e^{i(\omega_I q' + \omega_S p')\tau} F_j^{-(p+q)}(t) F_j^{-(p'+q')}(t-\tau)^* \right\rangle_{av} .$$

(III-32)

This expression is written by neglecting the cross-correlation of dipolar interaction between different pairs. This assumption is made without any a priori justification [35], for want of a better treatment. Further, since the magnetic energy levels designated by different S_z values are closely spaced compared to kT and since there is a very large number of 'j' nuclei to be summed over, it may be assumed that the neighbouring nuclei are evenly distributed amongst their $(2S+1)$ levels [ref. 36, p. 233]. By doing so we are effectively treating the spin \underline{S} as part of the "lattice" which is assumed to remain always in thermal equilibrium. This summation may then be carried over by replacing the product $S_j^p S_j^{-p'}$ by its expectation value $\delta_{p, p'} (|p|+1)S(S+1)/3$.

Using the correlation function for translational diffusion calculated under "extreme narrowing" assumption [ref. 7, p. 300, and 35], the spectral densities (III-32) are obtained as:

$$J_{\alpha\beta\alpha'\beta'}^{en} = \frac{4S(S+1)}{3} \frac{N\pi}{5aD} \gamma_I^2 \gamma_S^2 \frac{1}{h^2} \sum_q \frac{1}{(|q|+1)} \left\langle \alpha \left| I^q \right| \beta \right\rangle \left\langle \beta \left| I^{-q} \right| \alpha' \right\rangle ,$$

(III-33)

where N is the number of spins (or molecules, for this case) per unit volume, " a " is the radius of the assumed spherical molecule and D is the translation diffusion coefficient. The translation correlation time τ_0 is then given by $\tau_0 = 2a^2/D$. Equation (III-33) again represents a random field (compare Eq. III-23) having a mean square value:

$$f = \frac{S(S+1)}{3} \frac{N\pi}{5a^3} \gamma_I^2 \gamma_S^2 \hbar^2 \quad (\text{III-34})$$

Thus under "extreme-narrowing" approximation, and if the spin states of S_z can be assumed to be equally populated (high temperature approximation), the intermolecular dipole-dipole interaction can be approximated by a random field.

This conclusion remains unaltered if the spins are considered to be situated at a distance " b " from the centers of the spherical molecules. In this case the average distance of closest approach between the spins becomes different from the above value ($2a$) and further both translational and rotational diffusion contribute to the time dependence of this interaction. These two are compensatory effects. The correlation function calculated for this model, for $b \leq a/2$, by Hubbard [35] leads to an expression similar to (III-33) with a slightly modified value of mean square fields which are given by:

$$f = \frac{S(S+1)}{3} \frac{N\pi}{5a^3} \gamma_I^2 \gamma_S^2 \hbar^2 [1 + 0.233(\frac{b}{a})^2 + 0.15(\frac{b}{a})^4 + \dots] \quad (\text{III-35})$$

The second and third terms add to less than 7 per cent of the first term for $b = a/2$.

Correlations:- If there **is** more than one spin in the molecule, the interaction hamiltonian (III-31) will become:

$$\mathcal{H}'(t) = \sum_i \sum_j \sum_q I_i^q \sum_p C_p^q S_j^p F_{ij}^{-(p+q)}(t) \quad (\text{III-36})$$

where i stands for all nuclei in the molecule. The various terms ~~that~~ will occur in the calculation of spectral densities will be, in general, of the type:

$$\sum_{\substack{q, q' \\ p, p'}} (I_i^q C_p^q S_j^p)_{\alpha\beta} (I_{i'}^{q'} C_{-p}^{q'} S_{j'}^{p'})_{\beta'\alpha'} \left\langle F_{ij}^{-(p+q)}(t) F_{i'j'}^{-(p'+q')}^*(t-\tau) \right\rangle_{av} \quad (\text{III-37})$$

The terms for which $i = i'$ and $j = j'$ represent the completely correlated terms, included in the above calculations. The terms for which $j \neq j'$ represent cross-terms between dipolar interactions with external spins and may be assumed to be completely uncorrelated and taken as zero [35] (these terms are zero even when $i = i'$, but $j \neq j'$ and it is this part which was assumed zero in Eq. (III-32)). The terms for which $i \neq i'$ but $j = j'$ represent the field produced at the two spins i and i' in the molecule by the same external spin j and represent the case of partial

correlation. Noggle [14] has performed a calculation of this term by assuming only translational diffusion and neglecting the effects arising due to the spins being not at the centers of assumed spherical molecules, which also leads to $f(i) = f(i')$. It is further assumed that the surface of closest approach is an ellipsoid of revolution about the internuclear axis of the two spins i and i' having a semi-major axis $(r + h)$ and semiminor axis h , where $2r$ is the distance between the spins i and i' and h is the nominal distance of closest approach of spin j to any of the spins i (assumed equal for both). The calculation showed that for $h \gg r$, $C = 1$ and for $r > h$, $C \rightarrow 0$.

(b) Scalar Coupling:- Using the hamiltonian (III-10) and Eqs. (III-2,11) for the scalar coupling of a single spin \underline{I} with a spin \underline{S} having fast time dependence in its spin states due to fast quadrupole relaxation, and using Eq. (III-21), the spectral densities for this case are obtained as:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = 4\pi^2 J^2 \int_{-\infty}^{+\infty} d\tau \sum_{q,q'} \frac{e^{i\omega_I q\tau}}{(|q|+1)(|q'|+1)} \langle \alpha | I^q | \beta \rangle \langle \beta' | I^{q'} | \alpha' \rangle$$

$$\left\langle S^{-q}(t) S^{-q'}(t-\tau)^* \right\rangle_{av} \quad (III-38)$$

Assuming Bloch equations for the time dependence of spin \underline{S} (ref. 7, p. 310 and [3]), one obtains $q = -q'$ and :

$$J_{\alpha\beta\alpha'\beta'}^{nv} = \frac{4\pi^2 J^2 S(S+1)}{3} \sum_q \frac{2\tau(|q|+1)}{[1+(\omega_I - \omega_S)^2 \tau_q^2 (|q|+1)]} \frac{1}{(|q|+1)} \\ \langle \alpha | I^q | \beta \rangle \langle \beta' | I^{-q} | \alpha' \rangle \quad (\text{III-39})$$

Using extreme narrowing $(\omega_S \tau_c)^2 \ll 1$, where τ_c is the correlation time for molecular reorientation which causes the fluctuations in the electric field gradients at the site of spin S (this assumption has to be made for Bloch equations to hold for motion of spin S for $S > 1$, [3]), we obtain $\tau_1 = \tau_2 = \tau_q$ where τ_q is the quadrupole relaxation time of S . Equation (III-39) then represents a random field (compare Eq. II-22 and note $(\omega_I - \omega_S)^2$ instead of ω_I^2 in the denominator) with a mean square value:

$$f = \frac{4\pi^2 J^2 S(S+1)}{3} \quad (\text{III-40})$$

Thus the only condition for scalar coupling to be approximated as a random field is "extreme narrowing" for molecular reorientation, which is generally true. It may, however, be noted that $(\omega_I - \omega_S)^2 \tau_q^2$ is normally not less than unity and in fact quite often $(\omega_I - \omega_S)^2 \tau_q^2 \gg 1$ is obtained.

Correlations:- If there are number of $I(i)$ spins coupled to one S spin (having fast time dependence in its spin states) then the random fields at various $I(i)$ spins will

be completely correlated ($C = 1$) with mean square fields equal to $4\pi^2 J_{is}^2 S(S+1)/3$.

In case there are more than one spin of the type $\tilde{S}(j)$ (having fast time dependence) the portions of the fields produced at the site of any spin $\tilde{I}(i)$ by different $\tilde{S}(j)$ spins may be assumed to be completely uncorrelated with each other. This then leads to a case of partial correlation between the fields at various $\tilde{I}(i)$ spins with the extent of correlation governed by the coupling constants J_{ij} .

(c) Spin-Rotation Interaction:- Using the hamiltonian (III-18) and Eq. (III-21) the spectral densities are obtained as:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = \sum_{i,i'} \sum_{q,q'} (-1)^q \langle \alpha | A_i^q | \beta \rangle \langle \beta' | A_{i'}^{-q'} | \alpha' \rangle \int_{-\infty}^{+\infty} d\tau e^{-i\omega_I q' \tau} \left\langle F_i^q(t) F_{i'}^{q'}(t-\tau) \right\rangle_{av} \quad (III-41)$$

This expression has been evaluated by Hubbard [31], under the assumption that the characteristic time τ_1 for the change of the components of angular momentum J^q is very much different from τ_2 for molecular reorientation, as:

$$J_{\alpha\beta\alpha'\beta'}^{nv} = N \frac{1kT}{9\hbar^2} \sum_q \left\{ \frac{(2C_{\perp} + C_{\parallel})^2 2\tau_1}{[1 + (\omega_I q \tau_1)^2]} + \frac{2(C_{\parallel} - C_{\perp})^2 2\tau_{12}}{[1 + (\omega_I q \tau_{12})^2]} \right\} \frac{1}{(|q|+1)} \langle \alpha | I^q | \beta \rangle \langle \beta' | I^{-q} | \alpha' \rangle, \quad (III-42)$$

where

$$\frac{1}{\tau_{12}} = \frac{1}{\tau_1} + \frac{1}{\tau_2} \quad (\text{III-43})$$

and either $\tau_1 \ll \tau_2$ or $\tau_2 \ll \tau_1$. Here N is the number of identical I spins on the same molecule and kT is the Boltzmann factor. In writing expression (III-42), no correlation between spins on different molecules and complete correlation between spins on the same molecule are assumed [33].

Eq. (III-42) represents a sum of two random fields having different correlation times and different mean square fields. However if $\tau_1 \ll \tau_2$, $\tau_{12} \cong \tau_1$ and Eq. (III-42) gives a random field with mean square field as:

$$f = N \left(\frac{IkT}{9\hbar^2} \right) \left[(2C_{\perp} + C_{\parallel})^2 + 2(C_{\parallel} - C_{\perp})^2 \right] = N \frac{IkT}{3\hbar^2} (2C_{\perp}^2 + C_{\parallel}^2). \quad (\text{III-44})$$

IIIC TREATMENT OF SCALAR COUPLING AS A RELAXATION MECHANISM

When a spin $\frac{1}{2}$ nucleus is coupled by scalar coupling to a nucleus having spin $\gg 1$, this coupling generally does not appear as a splitting due to the rapid quadrupole relaxation rate of the latter. Depending on the relaxation time τ_q of the quadrupole nucleus and the magnitude of this coupling a broadening in the spectrum of spin $\frac{1}{2}$ nucleus is generally observed. When this coupling is entirely "washed out" [37] (no residual splitting remains and only broadening

is observed) the scalar coupling interaction is treated as a relaxation mechanism. In the following the conditions under which such a treatment of scalar coupling becomes valid are discussed.

The manner in which the coupling of \underline{I} ($I = \frac{1}{2}$) with \underline{S} ($S \gg 1$) affects the single resonance spectrum of spin \underline{I} can be treated by considering the total hamiltonian:

$$\mathcal{H} = \mathcal{H}_0^I + \mathcal{H}_0^S + \mathcal{H}_{sc} + \mathcal{H}_{qs}(t) + \mathcal{H}_1(t) + \mathcal{H}_I(t), \quad (\text{III-45})$$

where \mathcal{H}_0^I and \mathcal{H}_0^S are zeeman terms of spins \underline{I} and \underline{S} respectively, \mathcal{H}_{sc} is the scalar coupling between them, $\mathcal{H}_{qs}(t)$ is the interaction of the quadrupole moment of \underline{S} with fluctuating electric field gradients and is responsible for relaxation of spin \underline{S} , $\mathcal{H}_1(t)$ is the interaction of observing r.f. field with the spin system and $\mathcal{H}_I(t)$ represents mechanisms of relaxation of \underline{I} other than scalar coupling with \underline{S} . The equation of motion of the spin density-matrix σ can then be written as:

$$\frac{d\sigma}{dt} = -i[\mathcal{H}_0^I + \mathcal{H}_0^S + \mathcal{H}_{sc} + \mathcal{H}_1(t), \sigma] - [\sigma - \sigma_0]. \quad (\text{III-46})$$

This equation includes complete information regarding the dynamical behaviour of the spin system including spin \underline{S} . In order to describe the relaxation effects on a transition

($m(i) \rightarrow m(i')$) in the spectrum of spin \underline{I} , one considers simultaneous existence of off-diagonal elements of σ of the type $|m(i), m_s\rangle \leftrightarrow |m(i'), m_s\rangle$ for all different values of m_s , the eigenvalue of S_z . Furthermore, as may be seen from Eq. (III-39) that if $4\pi^2 J^2 \ll (\omega_I - \omega_S)^2$ and if the relaxation time τ_q of spin \underline{S} due to $\mathcal{H}_{qS}(t)$ is such that $(\omega_I - \omega_S)^2 \tau_q^2 \gg 1$, the terms like $(I_+ S_- + I_- S_+)$ in $\underline{I} \cdot \underline{S}$ will not contribute significantly to various relaxation matrix elements. In such a case *only the* term $J I_z S_z$ may be retained in \mathcal{H}_{sc} . With such an approximation and setting $\mathcal{H}_I(t) = 0$ in Eq. (III-46) an expression for $I = \frac{1}{2}$ and $S = 1$, for the line shape of the spectrum of spin \underline{I} , is obtained, with the relaxation time τ_q of spin \underline{S} as a parameter, as [38]:

$$I(x) = -\frac{2\eta}{2\pi J} \frac{(45 + \eta^2 + 5x^2\eta^2)}{225x^2 + \eta^2(34x^2 - 2x^4 + 4) + \eta^4(x^6 - 2x^4 + x^2)}, \quad (\text{III-47})$$

where $\eta = 10\pi\tau_q J$ and $x = \Delta\omega/2\pi J$, in which $\Delta\omega$ is the difference between the Larmor frequency of spin \underline{I} and the observing frequency. Equation (III-47), given by Abragam [7, p. 504], was also obtained through basically similar but slightly different arguments by Pople [39] following a general treatment of lineshape by Sack [40] and Anderson [41]. This equation describes the spectrum of spin \underline{I} for the entire range of values of τ_q . If $\eta^2 \ll 1$, Eq. (III-47) leads to:

$$I(\omega) = -\frac{2\eta}{2\pi J} \frac{45}{225x^2 + 4\eta^2} = \frac{-\frac{3}{2}(\frac{8}{3}\pi^2\tau_q J^2)}{(\Delta\omega)^2 + (\frac{8}{3}\pi^2\tau_q J^2)^2}, \quad (\text{III-48})$$

a lorentzian having a half-width at half-intensity equal to $8\pi^2\tau_q J^2/3$.

This is also the linewidth and lineshape obtained when scalar coupling is treated purely as a mechanism of relaxation with the condition that $(\omega_I - \omega_S)^2 \tau_q^2 \gg 1$. From the expression for spectral densities for scalar coupling mechanism Eq. (III-39), (assuming "extreme narrowing" for motion of spin \tilde{S}) one obtains for T_1 and T_2 of spin \tilde{I} :

$$\frac{1}{T_1} = \frac{8\pi^2 J^2 S(S+1)}{3} \frac{\tau_q}{1 + (\omega_I - \omega_S)^2 \tau_q^2} \quad (\text{III-49})$$

and

$$\frac{1}{T_2} = \frac{4\pi^2 J^2 S(S+1)}{3} \left(\frac{\tau_q}{1 + (\omega_I - \omega_S)^2 \tau_q^2} + \tau_q \right) \quad (\text{III-50})$$

From Eq. (III-50) it can be seen that, under the condition $(\omega_I - \omega_S)^2 \tau_q^2 \gg 1$ and for $S = 1$, the linewidth ($1/T_2$) is the same as in (III-48).

Thus the conditions under which scalar coupling can be treated as a relaxation mechanism are that $\eta^2 \ll 1$ and that "extreme-narrowing" holds for motion of spins \tilde{S} .

Equation (III-49), shows that if the above mentioned conditions i.e. $4\pi^2 J^2 \ll (\omega_I - \omega_S)^2$ and $(\omega_I - \omega_S)^2 \tau_q^2 \gg 1$ hold, the contribution of scalar coupling to $1/T_1$ becomes negligible and in that case the scalar coupling mechanism serves only as a source for spin-spin relaxation. The contact

of the spin system with the lattice is therefore primarily through other interactions in the sample.

IIID CROSS-TERMS BETWEEN VARIOUS INTERACTIONS

In a sample various interactions mentioned in the previous sections often simultaneously co-exist and it is only their relative importance that differs from sample to sample. In such a case there can exist cross-terms between different interactions in the calculation of spectral densities such as:

$$\left\langle \left\langle \alpha \left| \mathcal{H}_{sc}'(t) \right| \beta \right\rangle \left\langle \alpha' \left| \mathcal{H}_{dd}'(t) \right| \beta' \right\rangle^* \right\rangle_{av} \quad (\text{III-51})$$

besides cross-terms within an interaction. The cross-terms within an interaction have already been discussed under the title "correlations" in each case and in many cases found significantly important. The cross-terms between different interactions normally vanish because of either very different orders of magnitudes of time dependences involved in their hamiltonians, in which case the two parts can be separately averaged giving zero for the averages, or difference in transformation laws for each of the hamiltonians yielding zero on averaging [ref. 7, p. 309]. Specifically the cross-terms between scalar coupling and either of the dipole-dipole interactions or the random fields vanishes because of different orders of time-dependences involved.

Chapter IV

EXPERIMENTAL

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IV - EXPERIMENTAL

IVA FREQUENCY SWEEP DOUBLE RESONANCE SET-UP

1. Introduction

In homonuclear double resonance experiments the irradiated and the observed transitions belong to the same nuclear species, and therefore the frequencies of the irradiating and the observing r.f. fields differ by an audio-frequency. In such experiments the second r.f. field is produced by modulating the magnetic field with the appropriate audio frequency. Double resonance experiments can, in principle, be performed both by changing the magnetic field and keeping the frequency fixed (field sweep operation) or by keeping the magnetic field fixed and changing the frequency (frequency sweep operation). The frequency sweep experiments are convenient for relaxation studies and are used in the present work.

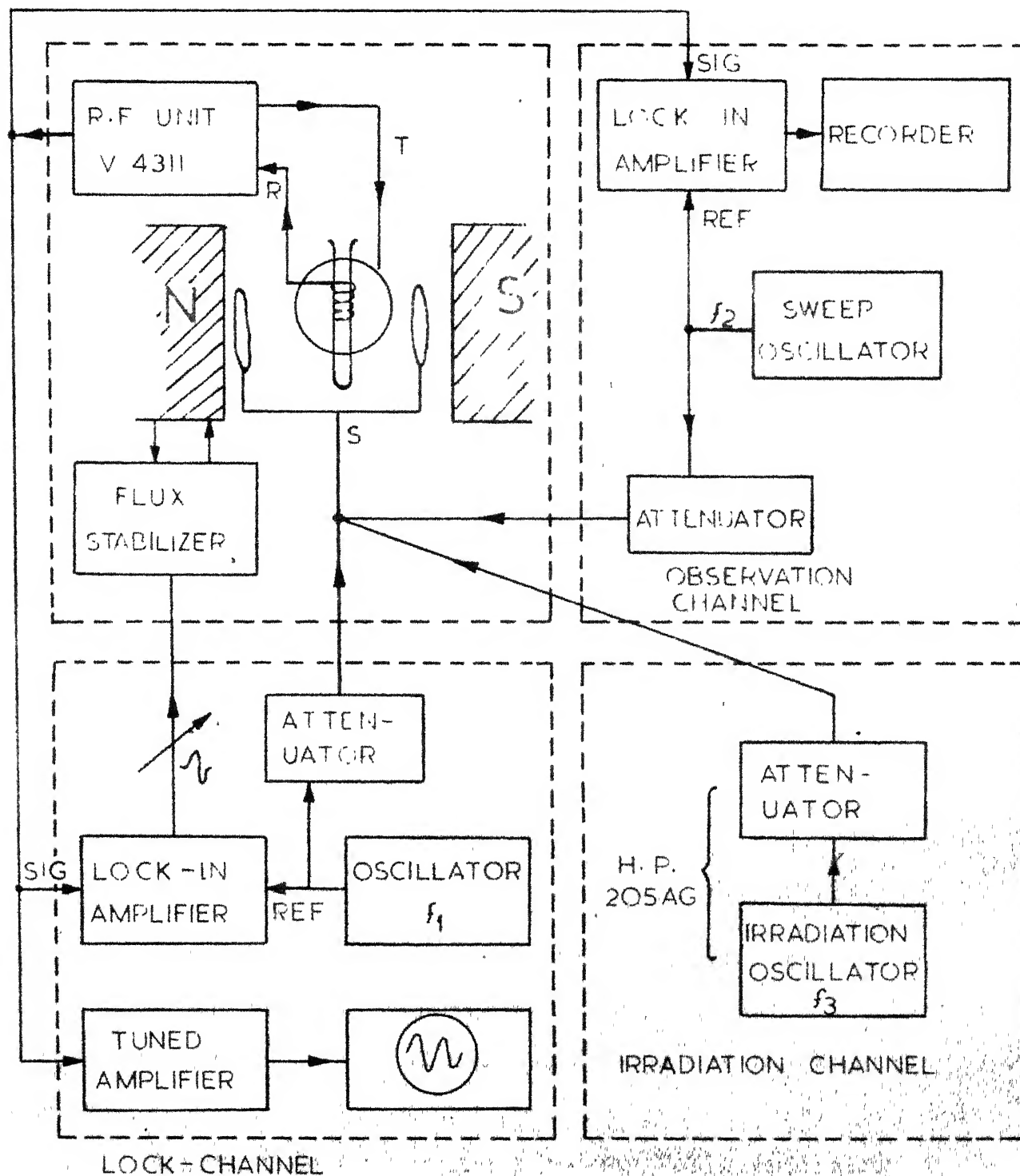
The conventional high resolution n.m.r. spectrometers, like the Varian HR-100, use field sweep operation. This instrument has been modified to perform frequency sweep single and double resonance experiments, by using field-frequency-locking-control loop [23,25]. Single resonance spectra have been obtained without loss of resolution and with improved stability, compared to field sweep operation. The modification, however, does not disturb the field sweep operation. The details of this modification are described in this section.

2. Basic Principle

In the first stage of this experiment the magnetic field is held fixed at a particular value. The experimental sample is added ~~with~~ a small amount of tetramethylsilane (TMS) which serves as a source of the locking signal. The magnetic field is modulated by an audio frequency f_1 , Fig. (IV-1), and is brought in resonance with the first low-field sideband of TMS. The output of the r.f. receiver is then phase detected through a lock-in-amplifier which is referenced by the same audio oscillator and has amplifiers tuned to frequency f_1 . The phase difference between the signal and the reference of the lock-in-amplifier is so adjusted that, as one sweeps through the resonance, the d.c. output of the lock-in-amplifier is obtained in the shape of an error signal. This error signal is fed to the flux-stabilizer such that it gives an appropriate correction voltage whenever the field drifts in either direction from its locked value. The output of the r.f. receiver is also monitored on a scope, after amplification through an amplifier tuned to frequency f_1 . A continuous steady display of a signal at f_1 indicates a locked field.

The single resonance spectrum is obtained by modulating the magnetic field by a second audio oscillator and sweeping its frequency (f_2) by a synchronous motor. When $f_2 = f_1 \pm \delta$, where δ is the frequency difference between the

Fig. IV-1. Block diagram of the experimental arrangement for a frequency sweep homonuclear double resonance set-up.



signal to be observed and TMS, the sideband of the signal will come in resonance with the locked field. The output of the receiver which now contains a component at f_2 also, is fed to another lock-in-amplifier which is referenced by the oscillator generating f_2 . This lock-in-amplifier is a broad-band amplifier. The output of the lock-in-amplifier is fed to a recorder. The sweep oscillator has a linear frequency dial so that the different parts of the spectrum are all scanned at the same rate and that the spectra are obtained with a linear frequency scale.

The irradiation of the spectrum is achieved by modulating the magnetic field with a third audio-oscillator (f_3) such that $f_3 = f_1 - \delta'$, where δ' is the frequency difference between the line to be irradiated and TMS. The amplitude of this oscillator is controlled by a calibrated attenuator.

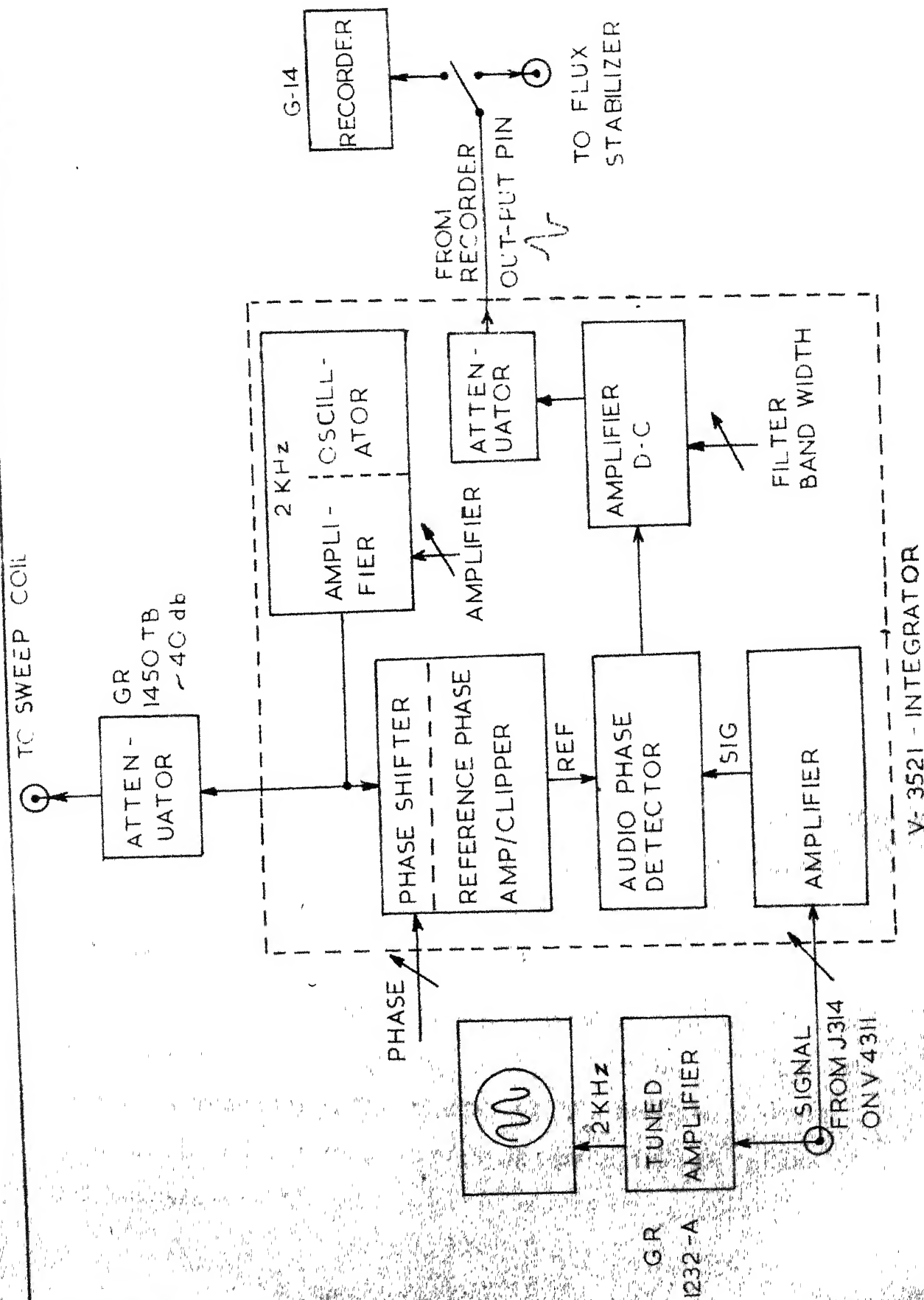
3. Details of the Experimental Arrangement

The high resolution n.m.r. spectrometer HR-100 consists of a 12" electromagnet (max. field 23.5×10^3 gauss) having a current regulated power supply. A flux stabilizer V3506 controls the time variations in the magnetic field while a field homogeneity control unit smoothens out any spatial variations of the field in the region of the sample. Crystal controlled r.f. transmitter and receiver V4311 operating at 100 MHz are used for proton resonance. The homogeneity and the stability of the magnetic field are ~ 1 in 10^8 . The resolution of the instrument is ~ 0.5 Hz. A linear sweep

unit V4352 giving a saw-tooth is used for scope presentation of the signal and a slow sweep unit V3507 which operates in conjunction with the flux stabilizer for slow recording of the spectrum in field sweep mode.

(a) Lock Channel:- The purpose of this channel is to hold the magnetic field H_0 fixed at a particular value. The 2 KHz audio-oscillator and lock-in-amplifier available in Varian V3521A integrator, have been used for this purpose Fig. (IV-2). The output of the audio-oscillator is attenuated by a GR 1450-TB attenuator, which serves as an isolation stage, before feeding to the sweep coils. Since the lock signal is derived from side-band resonance of TMS, the integrator is operated in "side-band" mode. The receiver output at J314 on V4311, which now contains an audio component at 2 KHz, is fed to the signal channel (referenced internally) through an attenuator. The phase difference between the reference and the signal can be adjusted with a front panel control. The output of the lock-in-amplifier, which is the error signal, is taken from the "recorder output" of the integrator and fed to the flux stabilizer through a switch. This error signal may be fed to pin 5 of J1 on the slow sweep unit. The amplitude and phase of the error signal are adjusted for maximum stability of the lock. The stability is monitored by feeding the output of the receiver at J314 to a scope, after amplification through a GR 1232A tuned amplifier tuned to f_1 . An amplitude of the order of 100 millivolts is usually needed for the error signal.

Fig. IV-2. Block diagram of the lock-channel. The components shown within the broken lines are available in the Varian integrator V3521.

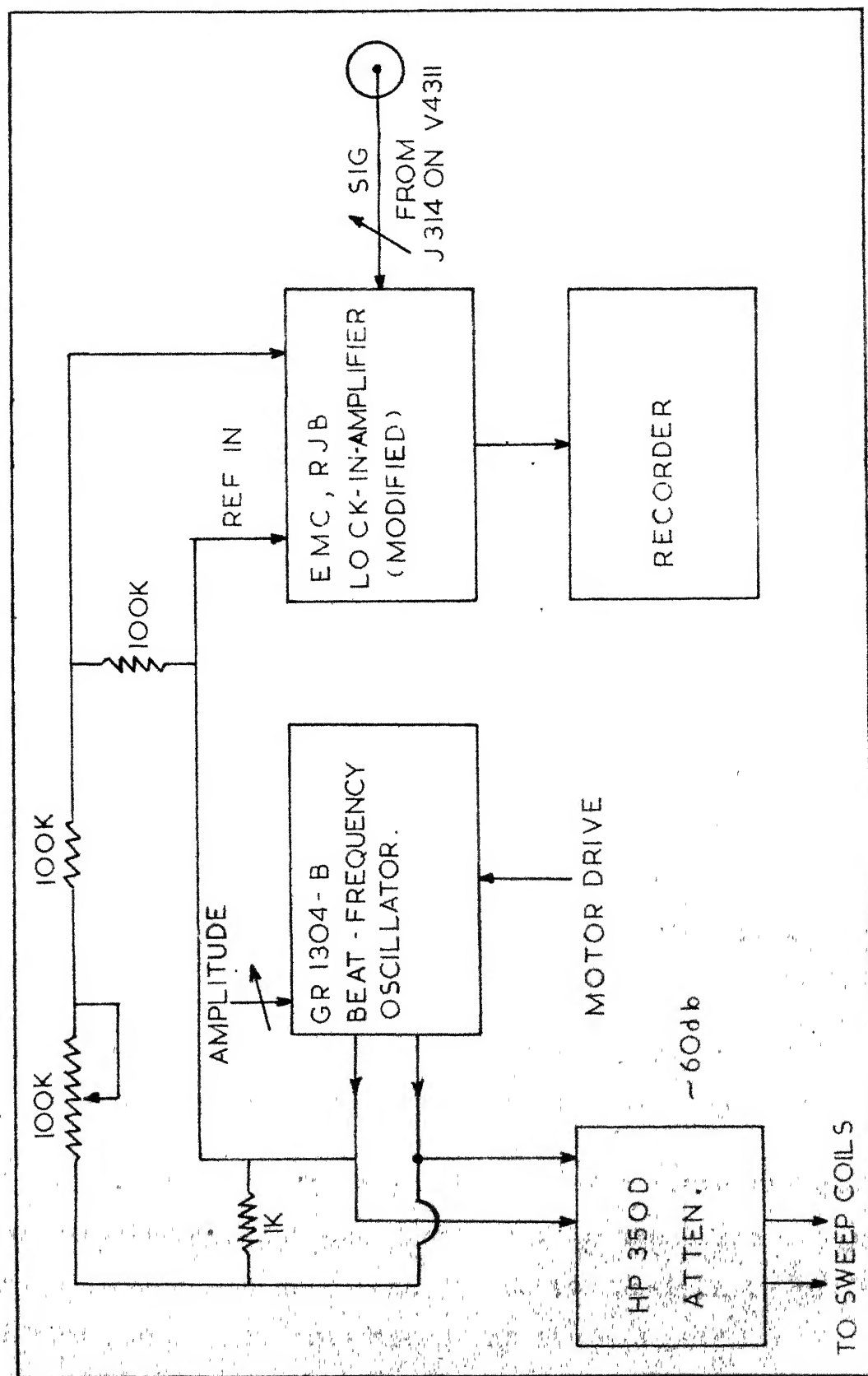


(b) Observation Channel:- A GR 1304-B, beat-frequency audio-oscillator, equipped with a linear increment dial (range 100 Hz) is used in this channel, Fig. (IV-3). The output of this oscillator is fed to the sweep coils at the modulation input jack on linear sweep unit through a HP 350-D attenuator. The lock-in-amplifier used in this channel is an 'EMC' (Electronics Missiles and Communications Inc. Mount Vernon, USA) model RJB. Since the input impedance of the reference channel of this lock-in-amplifier is $100\text{ K}\Omega$, the reference signal from beat-frequency oscillator is fed through a impedance matching net work.

The signal channel of the EMC lock-in-amplifier contains a negative feed back pentode amplifier which is heavily degenerative except at null frequency of a twin-tee net work, placed in the negative feed back circuit. Since the frequency is swept in the present experiment, this lock-in-amplifier is to be operated over a range of frequencies. These twin-tee's were, therefore, eliminated from the circuit and the screen grid of the pentode amplifier grounded, and as there is no degenerative feed back at any frequency the circuit acts as a broad band audio-amplifier.

The output of this lock-in-amplifier is obtained through a low frequency band pass filter and fed directly to a G-14 recorder. The phases of the frequency sweep spectra are adjusted by adjusting the reference phase of the EMC lock-in-amplifier.

Fig. IV-3. Block diagram of the observation channel.
An EMC, model RJB, lock-in-amplifier and a
GR 1304-B beat-frequency audio oscillator
are used in this channel.



(c) Irradiation Channel:- A HP 205-AG audio-oscillator has been used for irradiation. This oscillator has a maximum output power of 5 watts and a calibrated attenuator in its output. The output of this oscillator is fed at the modulation input jack on linear sweep unit.

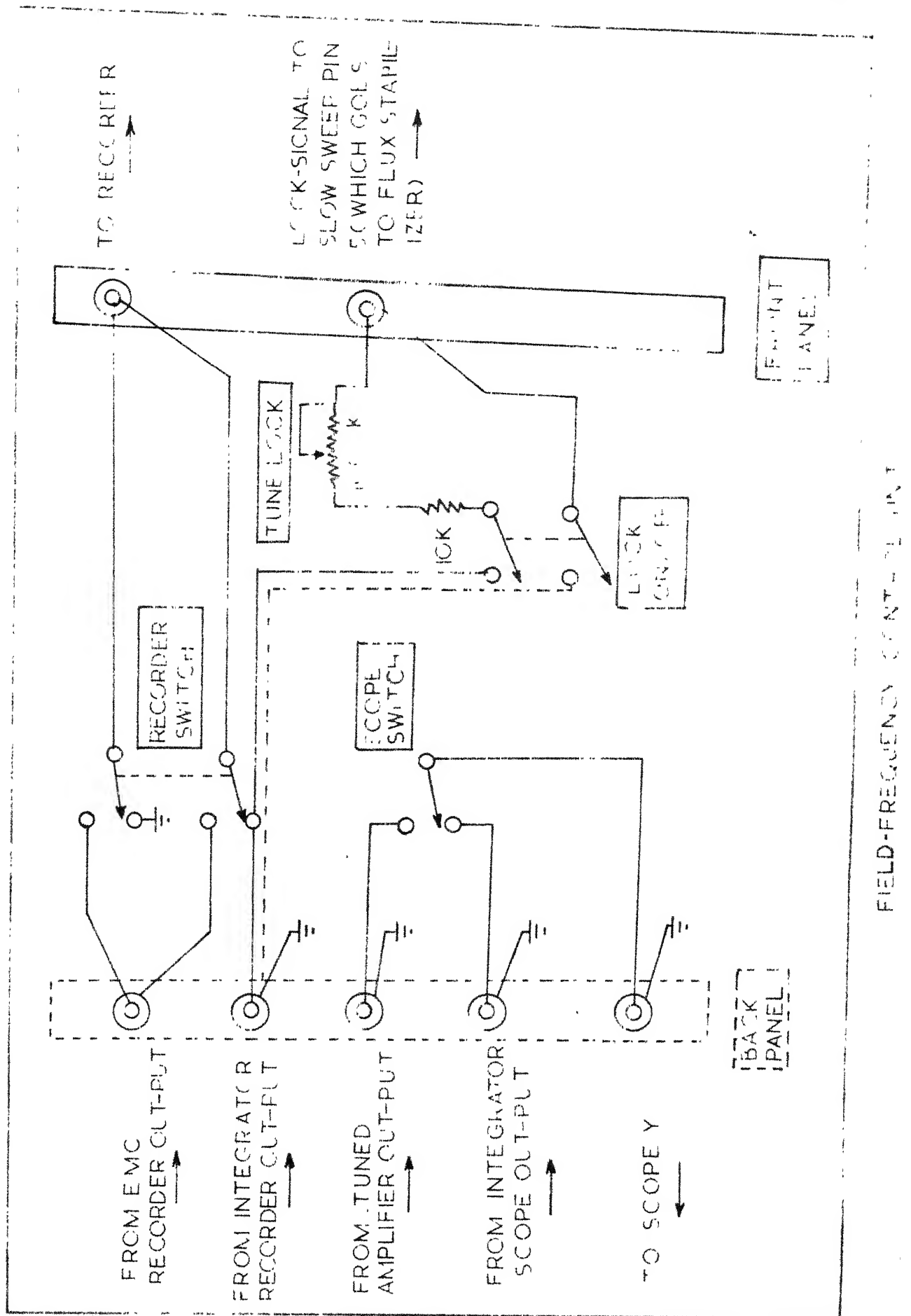
A HP 521C frequency counter is used for measuring frequencies of various audio oscillators.

(d) Field-frequency Control Panel:- A control panel essentially consisting of various switches, for a quick change from field-sweep operation to frequency sweep operation and vice-versa has been installed just below the oscilloscope. One switch, Fig. (IV-4), changes the input to the oscilloscope Y between integrator "scope output" and the tuned amplifier (2 KHz) output for monitoring the lock. Another switch changes the recorder from integrator "recorder-output" to ~~EMC~~ "recorder-output". One on/off switch is used for the error signal to the flux stabilizer. The amplitude of the error signal can be adjusted by the potentiometer "Tune lock".

If all the switches in this panel are flipped down the spectrometer is in the field-sweep mode.

(e) Operational Details:- The magnetic field is adjusted for best homogeneity and resolution in the field sweep mode and the low field side band of TMS ~~is~~ obtained in the shape of an error signal in this mode. At the mid point of this signal the sweep is taken off and the error signal fed to the

Fig. IV-4. Diagram showing the functions of various switches on the field-frequency control panel.



flux stabilizer. The sign of the error signal is chosen by trial and error by noting the locking or antilocking of the field. The lock is made stable by adjusting the amplitude of modulation and the amplitude of the error signal being fed to the flux stabilizer. A slight adjustment of the r.f. reference phase at V4311, has also been found useful for stabilizing the lock. The stability of the lock can be tested by deliberately trying to drift the field slowly and noting that the error signal compensates for it. Small variations in homogeneity are adjusted by maximising the output of f_1 at J314, which is monitored on the scope.

For the purpose of scanning the spectra the linear increment dial of the beat-frequency oscillator has been coupled to a synchronous motor through gears. Different driving speeds are obtained by changing the gear ratios.

The amplitude of the beat-frequency oscillator is usually kept large for the following reasons. As the input impedance of the reference channel of the EMC lock-in-amplifier is $100\text{ K}\Omega$, the output of ^{the} beat-frequency oscillator is first dropped across a $1\text{ K}\Omega$ resistance to match the output impedance of the oscillator and then dropped across a $100\text{ K}\Omega$ resistance to match the input impedance of the reference channel of EMC (Fig. IV-3). The two resistances are isolated by a $100\text{ K}\Omega$ potentiometer. The modulation amplitude of f_2 and the signal to the reference are adjusted respectively by the HP 350-D attenuator and the $100\text{ K}\Omega$

potentiometer. A large amplitude of the beat-frequency oscillator then ensures a high attenuator setting and a high value on 100 K Ω potentiometer. A high value of 100 K Ω potentiometer avoids any mismatching of the reference input impedance.

The frequency of irradiation is made to exactly coincide with a single resonance transition in the following manner. In the absence of irradiation the observing frequency f_2 , is swept to the peak of the line to be irradiated and the motor is then switched off. The amplitude of irradiation is then made fairly low (of the order of the amplitude of the observing **field**) and its frequency adjusted as near to f_2 as is possible with a frequency counter (within fraction of a Hz). At this stage the output of the EMC lock-in-amplifier will beat at the difference frequency of these two oscillators. This beat can be monitored either at output meter of the EMC lock-in-amplifier or on the recorder. The frequency of irradiation is now carefully adjusted by a fine control to reduce the beat frequency to zero, at which the EMC lock-in-amplifier will show a large d.c. amplitude as indicated by a large deflection of the output meter.

The irradiation oscillator is normally operated at full power and various amplitudes of irradiation^{are} obtained by using the calibrated attenuator. This facilitates (if all the other parameter are kept constant) a calibration of

complete range of strengths of irradiation once one of the values is calibrated.

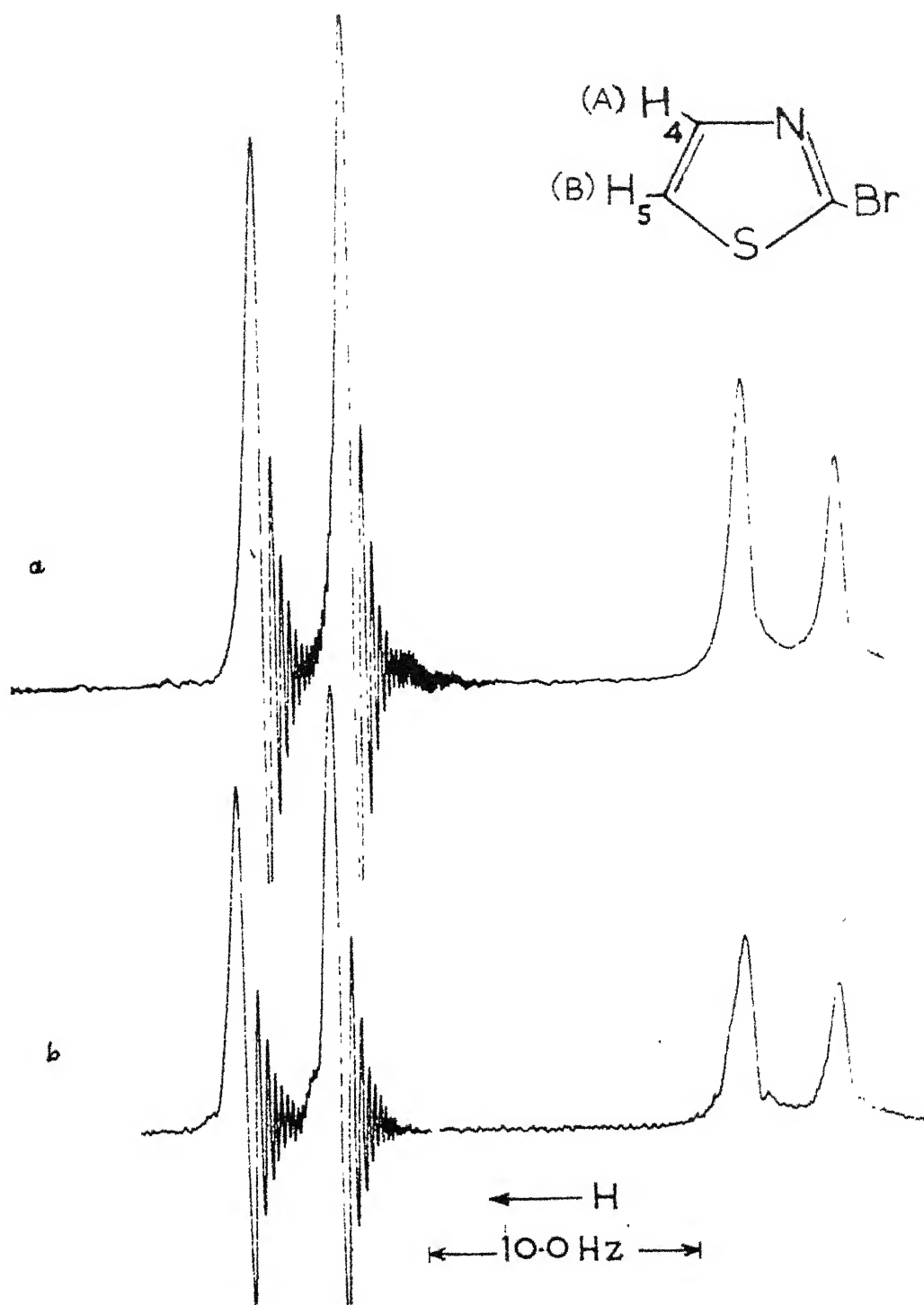
4. Performance

A comparison between the field-sweep single resonance proton spectrum of 2-bromothiazole and its frequency-sweep spectrum obtained with the above set-up is shown in Fig. (IV-5). The resolution in the frequency sweep operation is of the same order as the field sweep operation.

IVB SAMPLE PREPARATION

Commercial samples have been used in this work. The samples were purified, by recrystallizing in case of solid samples and redistillation in case of liquid samples, before sealing in 5 m.m. outer diameter n.m.r. sample tubes. A few drops of tetramethylsilane was added in each sample to provide the locking signal. The samples were degassed under vacuum by a series of freeze-pump-thaw cycles [14,22] and finally sealed in vacuum.

Fig. IV-5. The single resonance proton spectrum of 2-bromothiazole (a) in the field sweep operation and (b) in the frequency sweep operation obtained with the present set-up. The broader doublet is assigned to 'A' proton (position 4). The chemical shift between the two groups is $|\nu_A - \nu_B| = 18.8 \pm 0.1$ Hz and the coupling constant $J_{AB} = 3.55 \pm 0.05$ Hz.



Chapter V

DOUBLE RESONANCE STUDY OF PROTON RELAXATION IN A
SYMMETRICAL THREE SPIN SYSTEM (AB_2)

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V - DOUBLE RESONANCE STUDY OF PROTON RELAXATION IN A SYMMETRICAL THREE SPIN SYSTEM (AB₂)

VA INTRODUCTION

In this chapter the results of a proton-proton double resonance study of spin relaxation in a symmetrical three spin system (AB₂) formed by the ring protons of 2,6-dibromoaniline are presented. The sample consisted of a 20 per cent by weight solution of 2,6-dibromoaniline in CCl₄. Double resonance spectra exhibit significant relaxation effects over a wide range of strengths of irradiation (from 0.1 Hz to 9.0 Hz). The effect of magnetic field inhomogeneity on the linewidths of double resonance transitions has been explicitly considered in this analysis and is found to be of considerable importance in deriving information on the relaxation processes. Two relaxation mechanisms, (i) external isotropic random fields and (ii) internal dipole-dipole interactions between the ring protons along with possible correlations between them, have been considered for detailed calculations. The calculations for "high" strengths and "low" strengths of irradiation have been performed by the methods outlined in Chapter II. A detailed comparison of the calculated ^{spectra} Δ for both "high" and "low" strengths of irradiation with experiment is found to be essential for distinguishing between the contributions of the different mechanisms in this study.

VB SINGLE RESONANCE SPECTRUM

2,6-Dibromoaniline belongs to a symmetry point group C_{2v} and its ring protons form an AB_2 type of spin system (in the notation of Pople et.al. [2]). The resonance of proton "A" (in the para position with respect to NH_2 group) is expected to appear at a higher field than that of protons "B" (meta to NH_2 group)[†]. This gives $\nu_B > \nu_A$, where ν is resonance frequency. The basic-functions, diagonal and off-diagonal matrix elements of the spin hamiltonian and the transition frequencies and intensities for an AB_2 spin system are given in Table(V-1). The diagonal and off-diagonal matrix elements of double resonance hamiltonian in the rotating coordinate are also indicated in this table. In single resonance there are six symmetric and two antisymmetric spin functions, whose frequencies depend on two parameters viz. J_{AB} , the spin-spin coupling constant, and $|\nu_A - \nu_B|$ the chemical shift between the "A" and "B" protons.

The single resonance spectrum of the molecule is shown in Fig. (V-1). The spectrum has four well resolved "A" transitions and two closely spaced doublets in "B" transitions. The small separation in the two "B" doublets has been determined in the field sweep operation by "wiggle-beat"

† NH_2 is an electron donating group and produces greater chemical shielding at the site of the para proton than that of the meta proton in monosubstituted benzenes, while bromine is inactive in this respect [ref. 2, p. 259].

Table V-1A

Basic product functions, diagonal and off-diagonal matrix elements, wave-functions and energy values in single resonance† of an AB₂ spin system for which $|v_{OB}| > |v_{OA}|$.

S.N.	Basic product functions	F _Z ^{††}	Diagonal	Off-diag.	Wave-functions	Energy
1	$\alpha\alpha\alpha$	3/2	$\frac{1}{2}v_{OA} + v_{OB} + \frac{1}{2}J$		$\alpha\alpha\alpha$	$\frac{1}{2}v_{OA} + v_{OB} + \frac{1}{2}J$
2	$\beta\alpha\alpha$	1/2	$-\frac{1}{2}v_{OA} + v_{OB} - \frac{1}{2}J$	$\left. \begin{array}{l} \\ \end{array} \right\} J/\sqrt{2}$	$\cos\theta_+ \beta\alpha\alpha + \sin\theta_+ \alpha(\alpha\beta + \beta\alpha)/\sqrt{2}$	$\frac{1}{2}v_{OB} - J/4 + C_+$
3	$\alpha(\alpha\beta + \beta\alpha)/\sqrt{2}$	1/2	$\frac{1}{2}v_{OA}$		$-\sin\theta_+ \beta\alpha\alpha + \cos\theta_+ \alpha(\alpha\beta + \beta\alpha)/\sqrt{2}$	$\frac{1}{2}v_{OB} - J/4 - C_+$
4	$\beta(\alpha\beta + \beta\alpha)/\sqrt{2}$	-1/2	$-\frac{1}{2}v_{OA}$	$\left. \begin{array}{l} \\ \end{array} \right\} J/\sqrt{2}$	$\cos\theta_- \beta(\alpha\beta + \beta\alpha)/\sqrt{2} + \sin\theta_- \beta\alpha\alpha$	$-\frac{1}{2}v_{OB} - J/4 + C_-$
5	$\alpha\beta\beta$	-1/2	$\frac{1}{2}v_{OA} - v_{OB} - \frac{1}{2}J$		$-\sin\theta_- \beta(\alpha\beta + \beta\alpha)/\sqrt{2} + \cos\theta_- \beta\alpha\alpha$	$-\frac{1}{2}v_{OB} - J/4 - C_-$
6	$\beta\beta\beta$	-3/2	$-\frac{1}{2}v_{OA} - v_{OB} + \frac{1}{2}J$		$\beta\beta\beta$	$-\frac{1}{2}v_{OA} - v_{OB} + \frac{1}{2}J$
7	$\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	1/2	$\frac{1}{2}v_{OA}$		$\alpha(\alpha\beta - \beta\alpha)/\sqrt{2}$	$\frac{1}{2}v_{OA}$
8	$\beta(\alpha\beta - \beta\alpha)/\sqrt{2}$	-1/2	$-\frac{1}{2}v_{OA}$		$\beta(\alpha\beta - \beta\alpha)/\sqrt{2}$	$-\frac{1}{2}v_{OA}$

† For double resonance hamiltonian in the rotating frame, the basic product functions, the diagonal and off-diagonal matrix elements are same as given in this table with the modification that v_{OA} and v_{OB} are replaced by A_A and A_B respectively, and with additional off-diagonal elements $(\mathcal{H}_O^{RR})_{12} = \frac{1}{2}v_{2A}; (\mathcal{H}_O^{RR})_{13} = \frac{1}{2}v_{2B}; (\mathcal{H}_O^{RI})_{24} = \frac{1}{2}v_{2B}; (\mathcal{H}_O^{RI})_{35} = \frac{1}{2}v_{OB}; (\mathcal{H}_O^{RR})_{45} = \frac{1}{2}v_{2A}$ and $(\mathcal{H}_O^{RR})_{78} = \frac{1}{2}v_{2A}$ (see Eqs. I-3 and II-26). The diagonalization of this hamiltonian is done numerically by a computer.

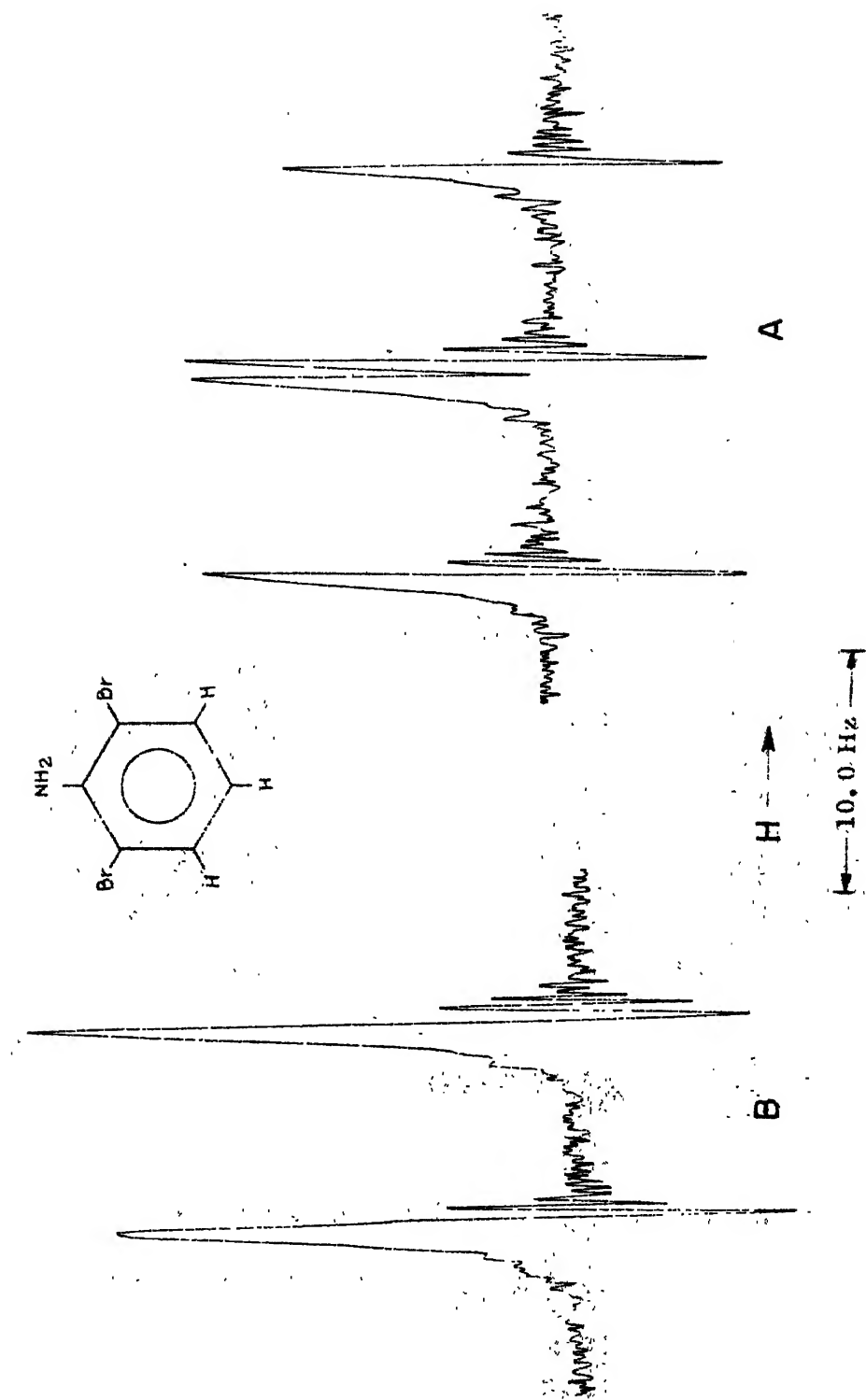
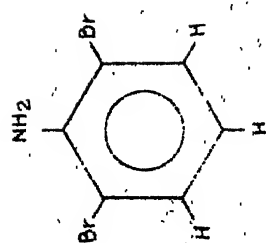
$$F_Z = \sum_I I_Z(i); C_{\pm} \cos 2\theta_{\pm} = \frac{1}{2}(v_{OB} - v_{OA}) \pm J/4; C_{\pm} \sin 2\theta_{\pm} = J/\sqrt{2}.$$

Table V-1B

The transition frequencies and intensities of single resonance transitions in an AB_2 spin system for which $|v_{OB}| > |v_{OA}|$.

S.N.	Transition	Type	Energy w.r.t. v_{OA}	Relative intensity
1	$5 \rightarrow 6$	A	$\frac{1}{2}(v_{OB}-v_{OA})-3J/4-C_-$	$(\cos\theta_- - \sqrt{2} \sin\theta_-)^2$
2	$3 \rightarrow 4$	A	$(v_{OB}-v_{OA})-C_+-C_-$	$[\cos\theta_+ \cos\theta_- + \sqrt{2} \sin(\theta_- - \theta_+)]^2$
3	$7 \rightarrow 8$	A	0	1
4	$1 \rightarrow 2$	A	$\frac{1}{2}(v_{OB}-v_{OA})+3J/4-C_+$	$(\sqrt{2} \sin\theta_+ + \cos\theta_+)^2$
5	$2 \rightarrow 4$	B	$(v_{OB}-v_{OA})+C_+-C_-$	$[\sqrt{2} \cos(\theta_- - \theta_+) + \sin\theta_+ \cos\theta_-]^2$
6	$4 \rightarrow 6$	B	$\frac{1}{2}(v_{OB}-v_{OA})-3J/4+C_-$	$(\sqrt{2} \cos\theta_- + \sin\theta_-)^2$
7	$3 \rightarrow 5$	B	$(v_{OB}-v_{OA})-C_++C_-$	$[\sqrt{2} \cos(\theta_- - \theta_+) - \sin\theta_- \cos\theta_+]^2$
8	$1 \rightarrow 3$	B	$\frac{1}{2}(v_{OB}-v_{OA})-3J/4-C_-$	$(\sqrt{2} \cos\theta_+ - \sin\theta_+)^2$

Fig. V-1. Frequency sweep single resonance spectrum of the ring protons of 2,6-dibromoaniline, which form an AB_2 type of spin system. The chemical shift between the two groups is $|\nu_A - \nu_B| = 89.95$ Hz and the coupling constant is $J_{AB} = 7.95$ Hz.



method [ref. 2, p. 76]. In this method if the separation between the lines in a doublet is J in cycles per sec., the time between successive beat maxima is equal to $1/J$ sec. The values obtained for this case are 0.3 ± 0.1 Hz and 0.4 ± 0.1 Hz respectively for high and low field doublets. The analysis of the single resonance spectrum is straight forward and the parameters obtained are $|\nu_A - \nu_B| = 89.95 \pm 0.1$ Hz and $J_{AB} = 7.95 \pm 0.1$ Hz.

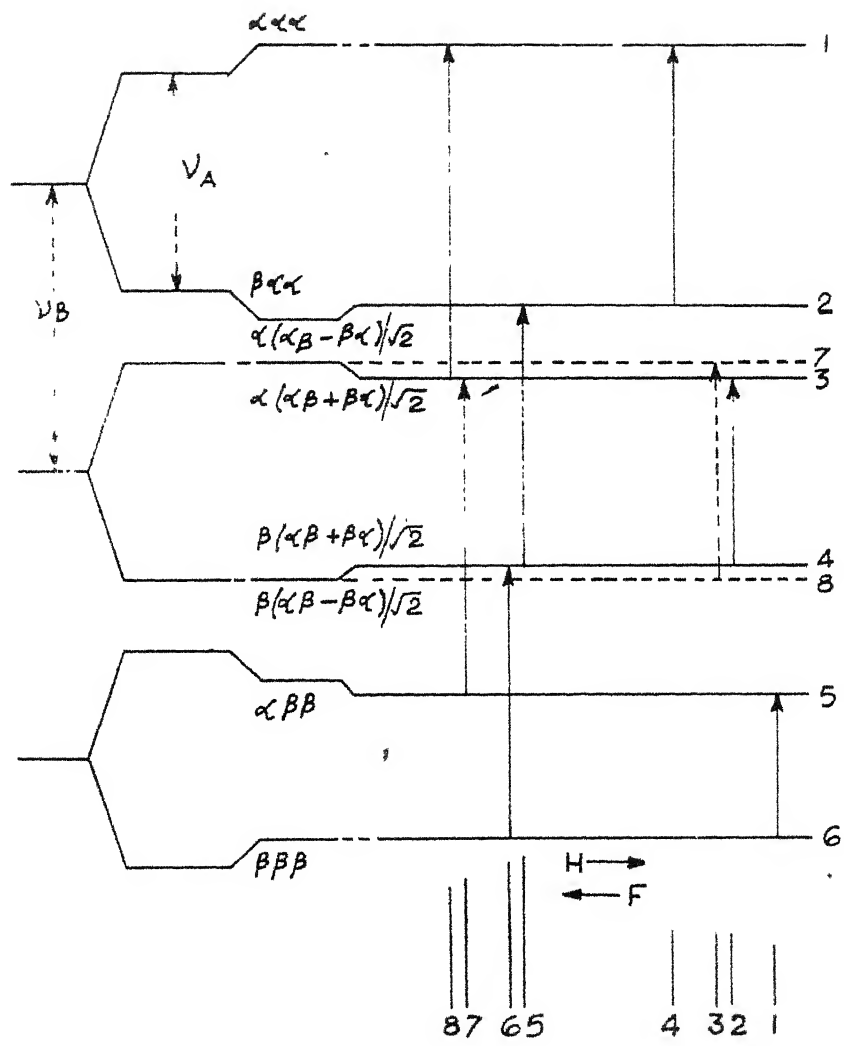
The different transitions are shown schematically with the help of an energy level diagram in Fig. (V-2) and are numbered in the order of increasing frequency. Lines 1 to 4 are "A" transitions and lines 5 to 8 are "B" transitions. Line 3 is the transition between the antisymmetric states $7 \rightarrow 8$.

VC DOUBLE RESONANCE SPECTRA

1. General Features

Double resonance spectra were obtained by irradiating each one of the lines of the single resonance spectrum, for values of the strength of irradiation, ν_2 varying between 0.1 Hz and 9.0 Hz. Some of the typical double resonance spectra are shown in Figs. (V-3 to 7). The spectra with "low" strengths of irradiation do not show any splittings but do show marked intensity changes compared to single resonance, while the spectra with "high" strengths of irradiation show all the features of double resonance spectra viz. line splittings, line shifts, intensity and

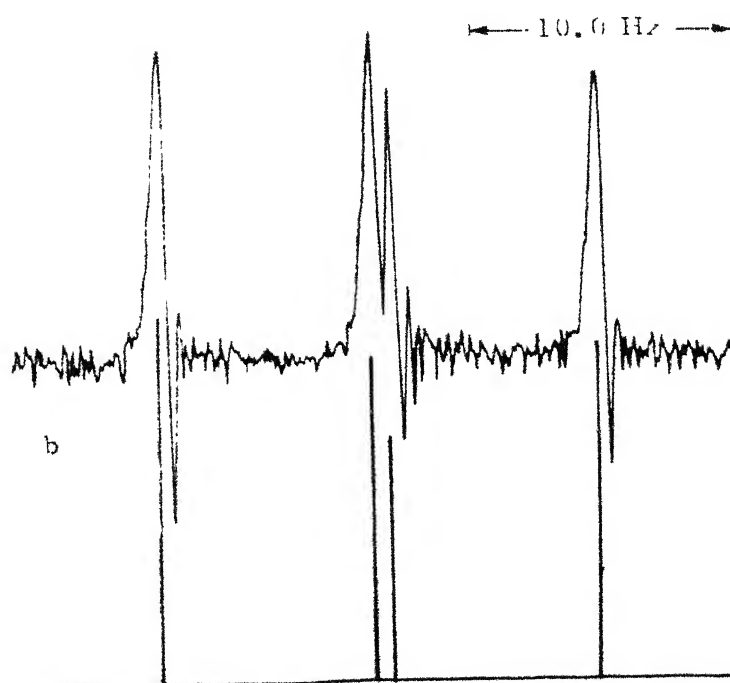
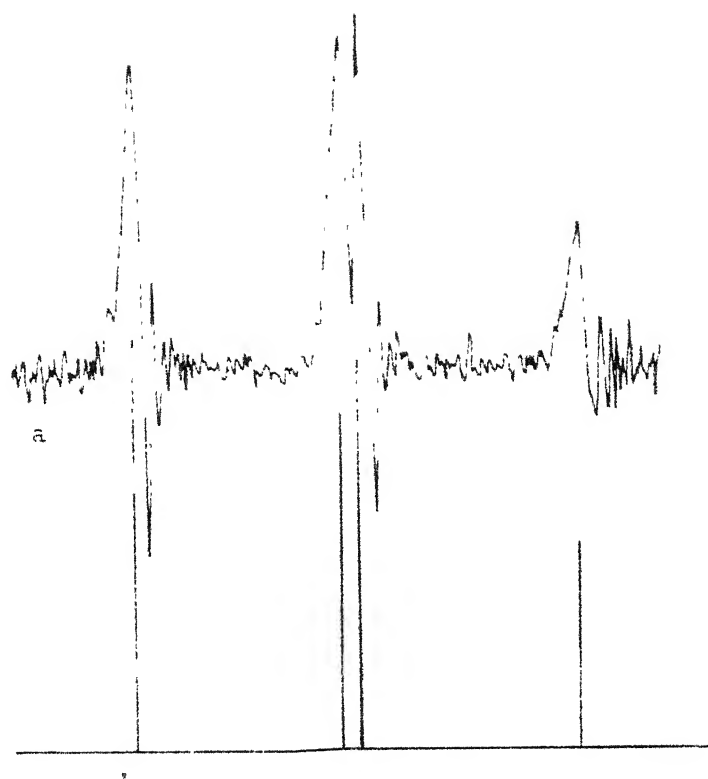
Fig. V-2. Energy level diagram of an AB_2 spin system for which $\nu_B > \nu_A$. The spin functions noted against different energy levels are the respective spin product functions. The various transitions are also shown schematically with heights proportional to the single resonance intensities. The lines 1 to 4 are 'A' transitions and the lines 5 to 8 are 'B' transitions. Line 3 is the transition between antisymmetric states 7 and 8.



linewidth changes. The values of ν_2 for spectra which show splittings were determined in the following manner. The hamiltonian in the rotating coordinate \mathcal{H}_0^R (Eq. II-26) is diagonalized by a computer for various values of ν_2 for any particular line of irradiation and the calculated line positions in the double resonance spectra plotted against ν_2 . These plots are then compared with the observed spectra for irradiation of that line [11]. This leads to a determination of ν_2 to an accuracy of ± 0.05 Hz. For cases of weak irradiation, low values of ν_2 were produced in the experiment by using a calibrated attenuator, and therefore for these spectra the values of ν_2 were calculated by multiplying the values determined for strong irradiation cases, by the respective attenuation factors.

The spectra for "low" amplitudes of irradiation exhibit the following general features. Figure (V-3(a)) shows the spectrum of "A" group while line 6 of "B" group is irradiated by an amplitude of 0.1 Hz. This produces a decrease in the intensity of line 1 and an increase in that of line 2. The corresponding spectrum for irradiation of line 7 (Fig. V-3(b)) shows a reverse effect in the intensities of lines 1 and 2. Both these features can be qualitatively understood by referring to the energy level diagram (Fig. V-2) and noting that the irradiation of a pair of levels causes an increase in the population of higher level and a depletion in that of the lower level. Therefore for irradiation of line 6 ($6 \rightarrow 4$ transition) the

Fig. V-3. Observed and calculated double resonance spectra of 'A' group in 2,6-dibromoaniline, while (a) line 6 and (b) line 7 of B group irradiated with an amplitude of 0.1 Hz. The calculated spectra are for random field mechanism (mechanism (i)) with $f(A)/f(B) = 2.0$, $C_{B_1B_2} = 1.0$, $C_{AB} = 0.0$ and $2f(B)\tau_c = 0.2$ rad./sec.



intensity of line 1 ($6 \rightarrow 5$ transition) should decrease while that of line 2 ($4 \rightarrow 3$ transition) should increase, in conformity with the observation (Fig. V-3(a)). These changes are reflected in ^{the} intensities of all those transitions in the spectrum which have an energy level in common with the pair being irradiated[†]. Similar intensity changes have also been observed for weak irradiation of other lines except line 3. Typical cases of "B" spectra when lines in "A" group are irradiated with $\nu_2 = 0.1$ Hz are shown in Fig. (V-4).

A weak irradiation of line 3, which is the transition between the antisymmetric states, does not produce intensity changes in other lines^{††} and furthermore in any of the observed double resonance spectra (Figs. V-3, 5 and 6)

† Intensity changes, smaller than the above, can also occur in the other transitions which are connected by relaxation processes to the irradiated pair. These changes are not obvious from an inspection of the spectrum but may become significant for understanding the spectrum on a quantitative basis.

†† Intensity changes and splittings occur for irradiation of this line for large values of ν_2 , due to the fact that the symmetric states belong to the neighbouring transitions (particularly line 2 ($4 \rightarrow 3$ transition)), get perturbed by the irradiation.

Fig. V-4. Observed and calculated double resonance spectra of $^*B^*$ group in 2,6-dibromoaniline, while (a) line 1 and (b) line 4 of $^*A^*$ group are irradiated with an amplitude of 0.1 Hz. The calculated spectra are for random field mechanism with $f(A)/f(B) = 2.0$, $C_{B_1B_2} = 1.0$, $C_{AB} = 0.0$ and $2f(B)\tau_c = 0.2$ rad./sec.

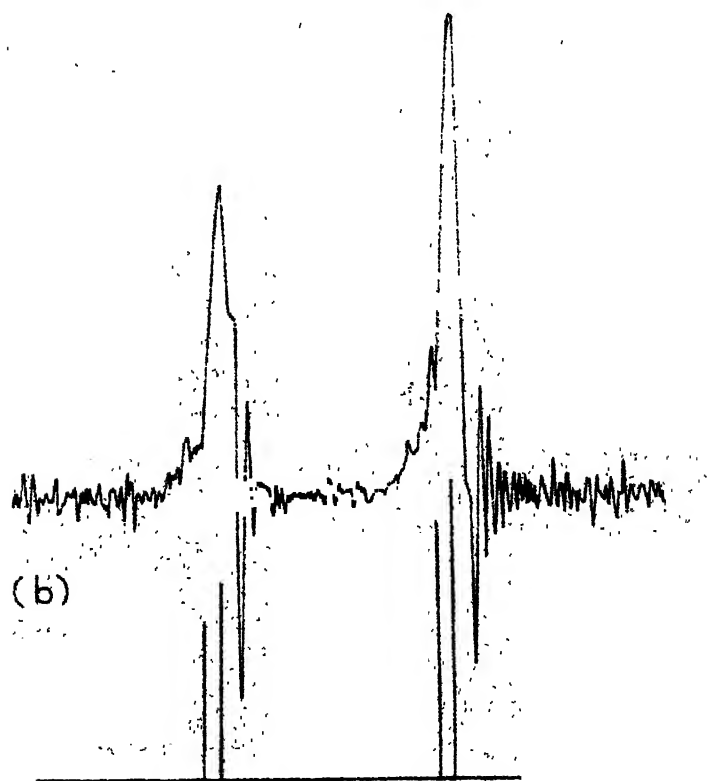
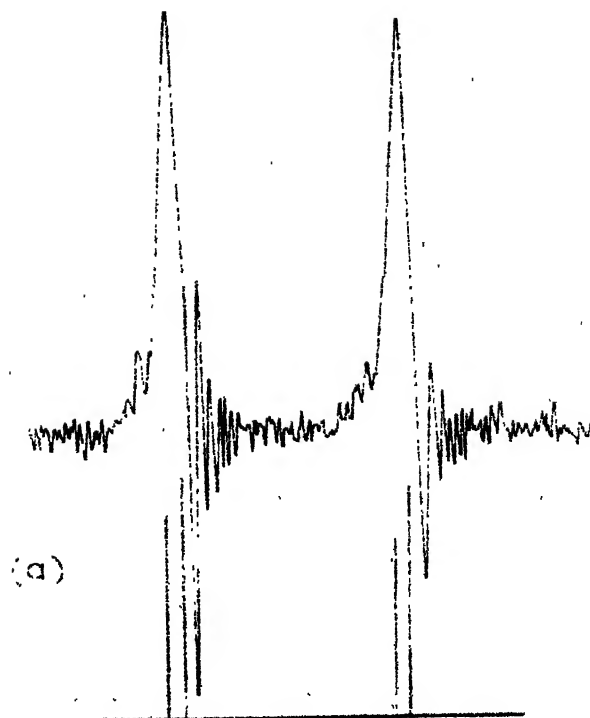


Fig. V-5. Observed and calculated double resonance spectra of $^*A'$ group in 2,6-dibromoaniline, while (a) line 6 and (b) line 7 of $^*B'$ group are irradiated with an amplitude of 2.2 Hz. The calculated spectra are for random field mechanism with $f(A)/f(B) = 2.0$, $C_{B_1B_2} = 1.0$ and $C_{AB} = 0.0$.

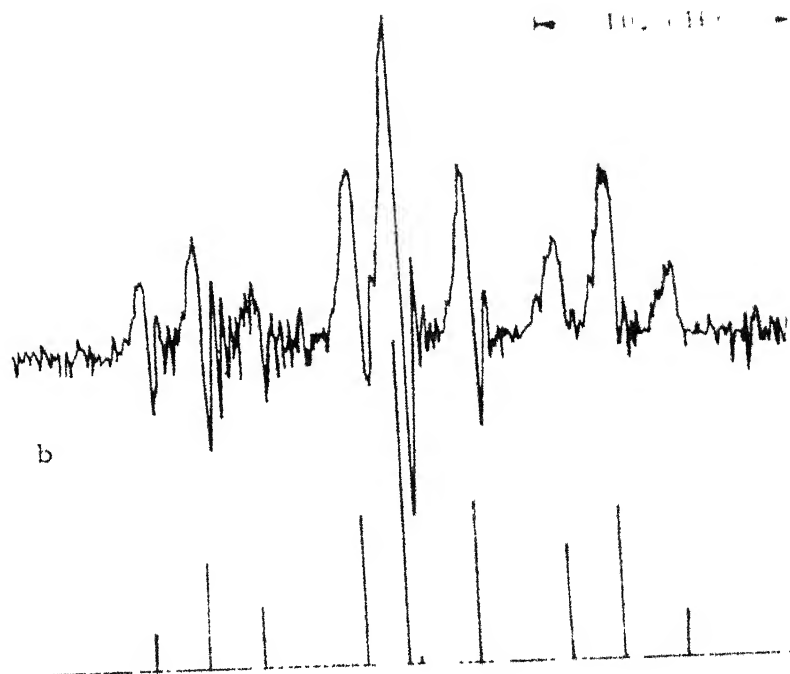
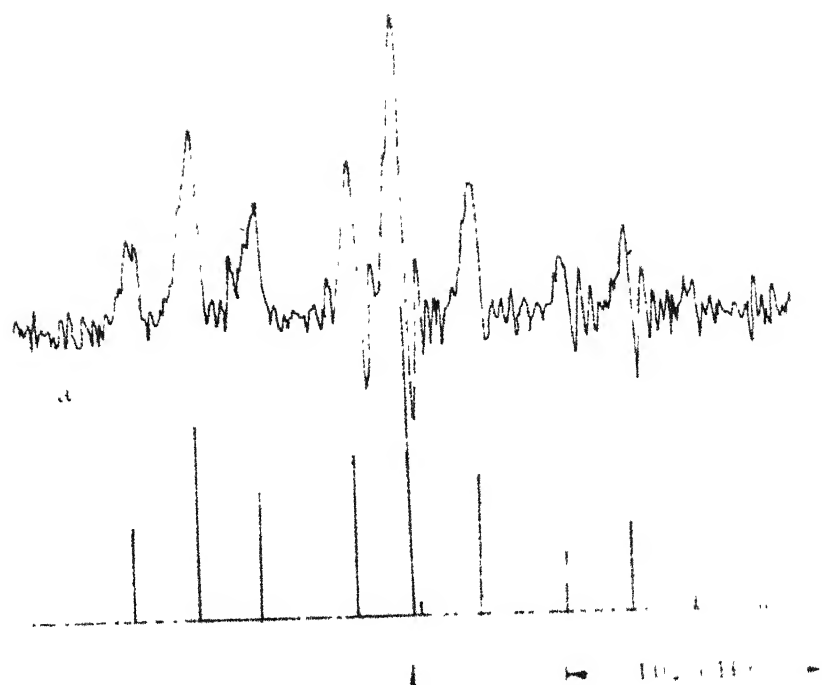


Fig. V-6. Observed and calculated double resonance spectra of 'A' group in 2,6-dibromoaniline, while (a) line 6 and (b) line 7 of 'B' group are irradiated with an amplitude of 6.75 Hz. The calculated spectra are for random field mechanism with $f(A)/f(B) = 2.0$, $C_{B_1B_2} = 1.0$ and $C_{AB} = 0.0$.

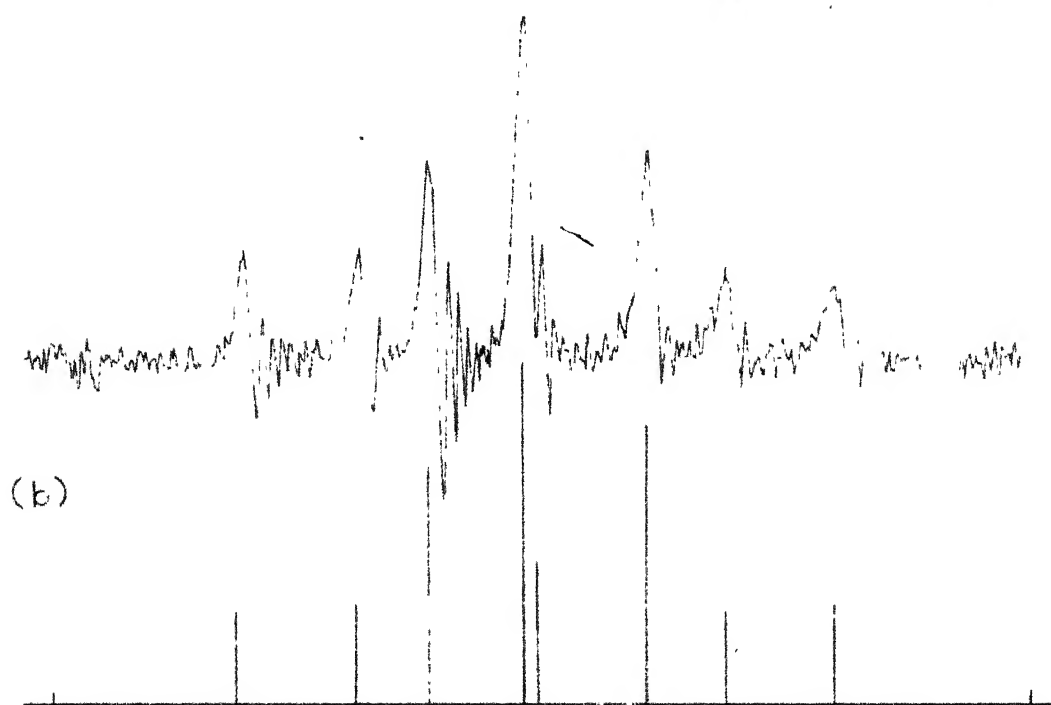
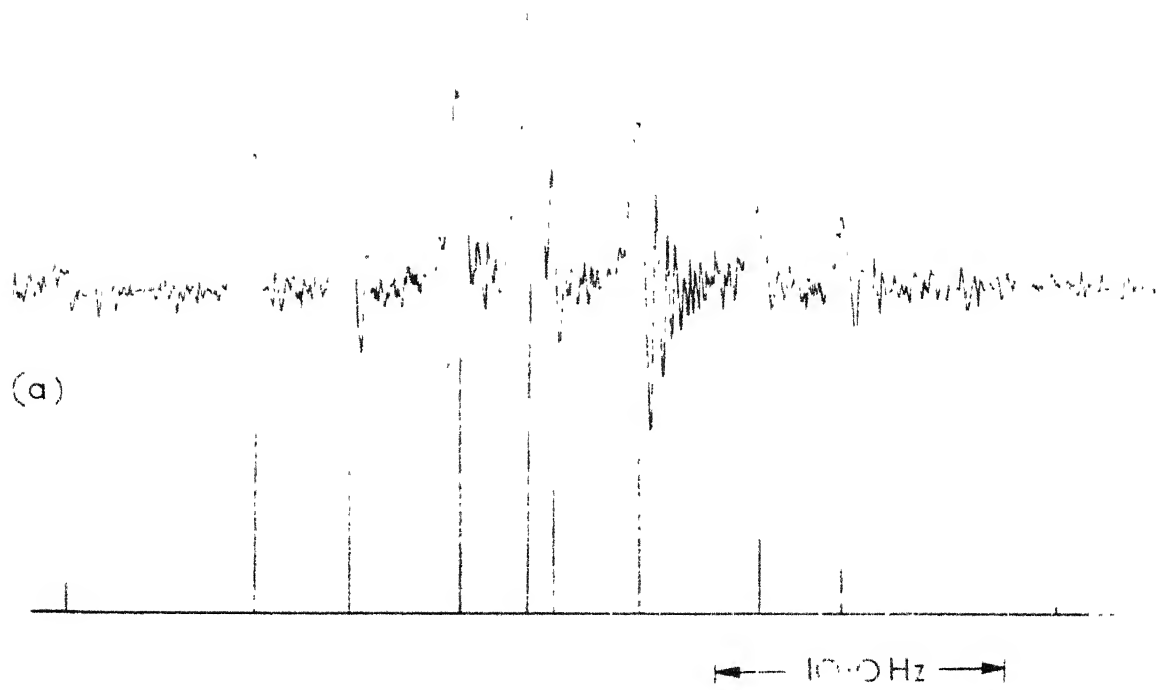
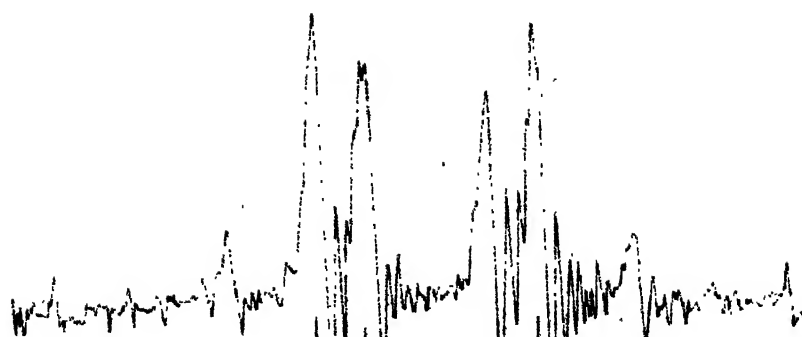
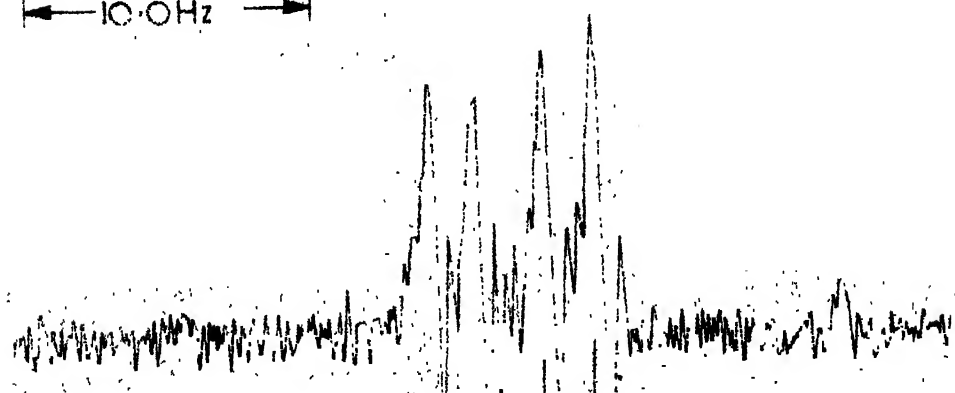


Fig. V-7. Observed and calculated double resonance spectra of 'B' group in 2,6-dibromoaniline, while (a) line 1 and (b) line 4 of 'A' group are irradiated by amplitudes of 5.25 Hz and 9.25 Hz respectively. The calculated spectra are for random field mechanism with $f(A)/f(B) = 2.0$, $C_{B_1B_2} = 1.0$ and $C_{AB} = 0.0$.



(a)

10.0 Hz



(b)

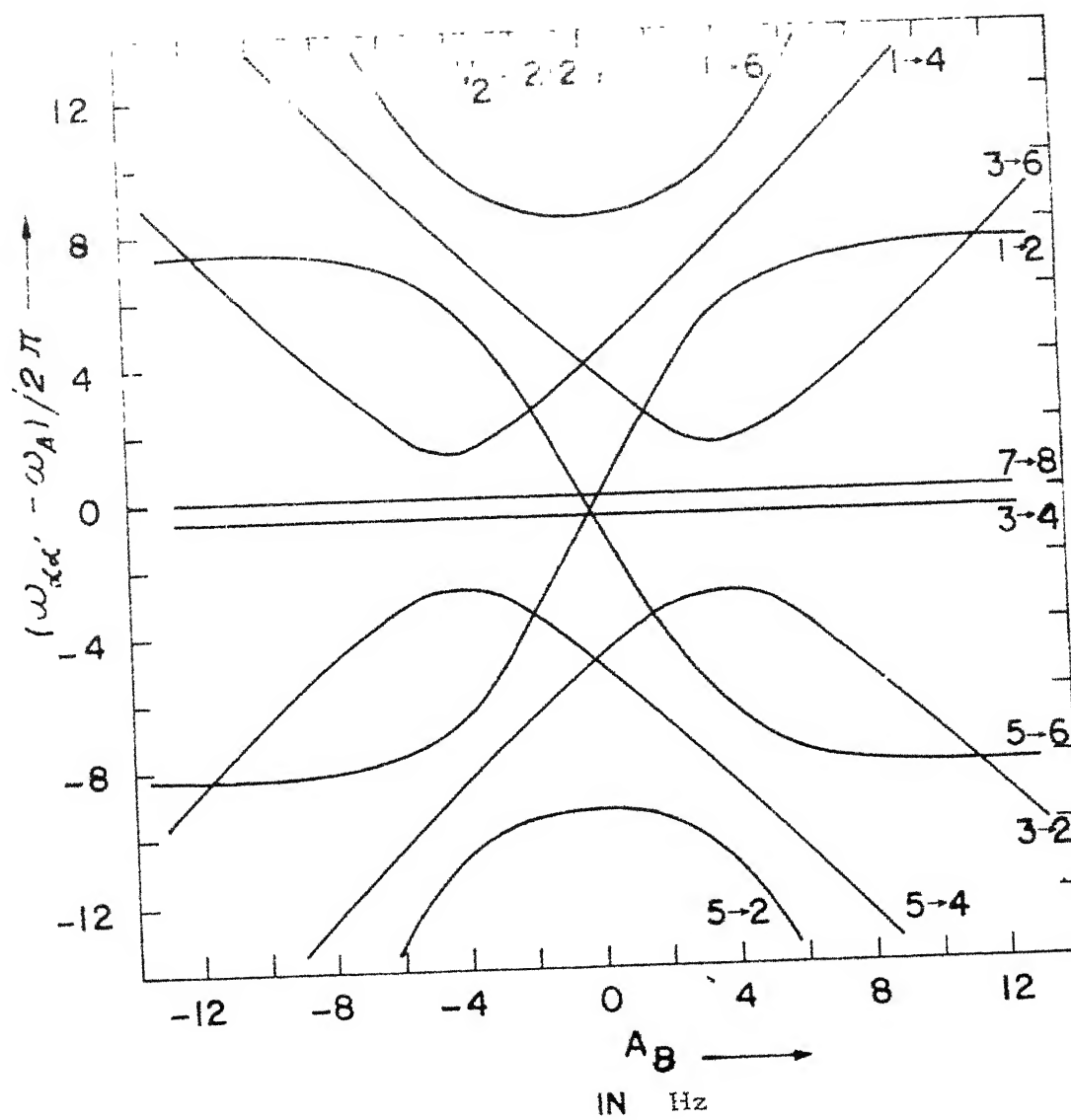
the intensity of this line is not changed[†]. This indicates that the relaxation hamiltonian does not connect the symmetric and antisymmetric states.

2. Linewidths

The double resonance spectra also exhibit significant linewidth variations. For example the spectrum of 'A' proton obtained when line 6 of the spectrum of 'B' proton is irradiated by an amplitude of 2.2 Hz (Fig. V-5(a)), has two triplets nearly symmetrical in frequency with respect to center, but having considerable difference in their linewidths. This asymmetry gets exactly reversed when line 7 is irradiated by the same amplitude (2.2 Hz) (Fig. V-5(b)). It was pointed out in Sec. (IIB-2) that the inhomogeneity in the static magnetic field can contribute differently to various transitions in the double resonance spectrum and that this contribution to any transition $\alpha \rightarrow \alpha'$ may easily be obtained from the plot of $\omega_{\alpha\alpha'}/2\pi$ versus A_j for weakly coupled spin systems. For making this estimate the present system may be considered as a weakly coupled system to a good approximation ($J/|\nu_A - \nu_B| \approx 0.09$). A plot of the frequencies of the 'A' transitions $(\omega_{\alpha\alpha'} - \omega_A)/2\pi$ versus $A_B = (\omega_2 - \omega_B)/2\pi$ for $\nu_2 = 2.2$ Hz, is shown in Fig. (V-8). These plots are constructed by diagonalizing \mathcal{H}_0^R with the help of the

[†] Line 3, therefore serves the useful purpose of being an intensity reference in the double resonance spectra.

Fig. V-8. Plots of calculated double resonance frequencies of 'A' transitions versus "frequency-offset" of irradiation of 'B' nuclei. These plots are calculated for the AB_2 spin system for $\nu_2 = 2.2$ Hz. The numbering of the states, corresponding to the transitions, is such that for large positive values of A_B and $\nu_2 = 0.0$, these states become the single resonance states as indicated in Fig. V-2.



computer and determining the corresponding transition frequencies for different values of A_B , keeping ν_2 constant. In joining the calculated points to construct these plots certain non-crossing rules [42] should be obeyed†. The transition frequencies in a frequency-sweep spectrum for any value of A_B are given by the points of intersection of an ordinate, drawn passing through that point, with the contours of Fig. (V-8). According to Eq. (II-63) the change in the contribution of the inhomogeneity to the width of a particular transition is then determined by the slope of the corresponding contour at the point of intersection. It may be seen from Fig. (V-8) that the frequency of the transition between the antisymmetric states $7 \rightarrow 8$ is not changed, due to a change in A_B , giving a zero slope for this line. This is a consequence of the fact that the irradiation does not mix states of different symmetry. This line (line 3) will then have the same contribution of inhomogeneity to the line-width as in single resonance. The frequency of the transition $3 \rightarrow 4$, which is weak in intensity, changes very little with A_B , since the coupling between A and B nuclei is not very strong in this case. In a weakly coupled spin system AX_2 , this line merges with $7 \rightarrow 8$ [43] and does not show frequency

† An operational statement of the non-crossing rule is: two contours belonging to two transitions which have an energy level in common will not cross in the presence of a perturbation.

shifts. However, in a strongly coupled AB_2 spin system it should show frequency shifts.

Irradiation of line 6 corresponds to $A_B = 3.6$ Hz. From the slopes of different contours in Fig. (V-8), at this value of A_B , it can be seen that for transitions $5 \rightarrow 2$, $5 \rightarrow 4$ and $5 \rightarrow 6$, forming the low-frequency triplet, the inhomogeneity broadening is mostly reduced while it is increased for transitions $1 \rightarrow 2$, $1 \rightarrow 4$ and $1 \rightarrow 6$, forming the high-frequency triplet in the same spectrum, in agreement with observation (see Fig. V-5(a)). Through a similar argument it is readily seen that this asymmetry is reversed when line 7 is irradiated, which corresponds to $A_B = -3.9$ Hz (see Fig. 5(b)). It may further be seen from this plot that at these ordinates the slope is nearly, +1 for various transitions for which there is a increase and -1 for those for which there is an recovery in the inhomogeneity contributions. This gives an inhomogeneity contribution of $2\gamma\Delta H_0$ to the linewidth of the former and nearly zero for the latter. For transitions $3 \rightarrow 6$ and $3 \rightarrow 2$ the slopes at these ordinates are almost zero (Fig. V-8) giving the contribution of inhomogeneity to the linewidths of these transitions same as in the single resonance. Making use of these observations, and the observed linewidths for irradiation of lines 6 and 7 with $\nu_2 = 2.2$ Hz, and the arguments of Sec. IIB-2(c), a value of $(\gamma\Delta H_0)/\pi$ is obtained to be about between 0.15 Hz - 0.18 Hz (full-width at half height).

3. Calculation of Relaxation Effects

The theoretical double resonance spectra were calculated according to the theory sketched in Chapter II for two relaxation mechanisms, (i) isotropic external random fields and (ii) internal dipole-dipole interactions, the interaction hamiltonians and expressions for correlation constants for which have been given in Sec. IIIA. The spectra for large values of the strength of irradiation ($|\gamma H_2| \gg |\sqrt{\alpha\alpha}|$) are calculated using the Bloch approximation. For 'low' strengths of irradiation, in which only intensity changes were observed and no line splittings and shifts occur, a solution for χ is obtained in the laboratory frame.

In the calculations for mechanism (i) the mean-square values of the fields at the different nuclei, the correlation between these fields and the value of τ_c , the correlation time, are the unknown factors in the absolute values of the elements of the relaxation matrix. For mechanism (ii) τ_c is the only unknown factor.

For mechanism (i), a fit with the observed spectra for strong irradiation can be obtained by performing the calculations for different values of $f(i)/f(i')$ (see Eq. III-4) and C_{ii} (see Eq. III-5). It has been pointed out in the previous section that the behavior of line 3, in the double resonance spectra obtained under different conditions, indicates that the relaxation mechanism in the molecule does not connect symmetric and antisymmetric states. The

relaxation mechanism, therefore, seems to preserve the equivalence of the two 'B' nuclei implied by the spin hamiltonian. For relaxation due to external random fields, the equivalence of the nuclei will be maintained if the random fields at their sites are such that $F_{B_1}^q(t) = F_{B_2}^q(t)$. This leads to the condition that the random fields at B_1 and B_2 are equal and completely correlated [16]. On the basis of this observation the calculations for mechanism (i) were performed by setting $f(B_1) = f(B_2) = f(B)$ and $C_{B_1 B_2} = 1$, and varying only the two quantities $f(A)/f(B)$ and C_{AB} , for high-field spectra[†].

For mechanism (ii) the factors $\frac{1}{2}(3\cos^2\psi_{NN'} - 1)$ which determine the correlations between the different pairs of spins (see Eq. III-9) are calculated assuming the geometrical arrangement of the three spins in 2,6-dibromoaniline to be the same as in an unsubstituted benzene molecule. The angle $\psi_{NN'}$ in benzene is 30° , 30° and 120° , giving 0.625, 0.625 and -0.125 for correlation between $(AB_1, B_1 B_2)$, $(AB_2, B_1 B_2)$ and (AB_1, AB_2) respectively. The distance between the protons is obtained (from the geometry of benzene) as 2.48 \AA between

+ It has been noticed in the computation that if $f(B_1)$ is set equal to $f(B_2)$, a variation in $C_{B_1 B_2}$ does not produce appreciable deviation in the intensity of line 3 from its single resonance intensity. The relative intensity and the linewidths of other transitions in the double resonance spectrum are also insensitive to this constant as will be shown by a later table (see Table V-5). Thus even though $C_{B_1 B_2}$ is set equal to unity to conform to the theoretical requirements on the complete equivalence of the 'B' nuclei, the experimental results do not allow an accurate estimate of this constant.

A and B protons and 4.29 Å° between B protons.

For every set of parameters describing the relaxation process the $\tilde{\chi}$ matrix is obtained and substituted in Eq. (II-59) to obtain the peak signal intensity. All the other quantities in the numerator of that expression are obtained by diagonalizing \mathcal{H}_0^R and calculating the matrix elements of $I_{\pm}(i)$ and σ_0 in that basis. It should be noted that the denominator in this expression contains the total linewidth including contributions from inhomogeneity and instability as discussed earlier. This amounts to substituting for $(\Delta\omega)_{\alpha\alpha'}$ in Eq. (II-59) just the value of the observed linewidth to obtain the value of $S_{\alpha\alpha'}^+ p$.

VD DISCUSSION

The calculated relative intensities in the double resonance spectrum for mechanism (i) with three different values 1.5, 2.0 and 2.5 for $f(A)/f(B)$ and $C_{AB}=0.0$ for all the three cases, and those for mechanism (ii) are given in Table (V-2) along with the observed relative intensities for the cases of irradiation of line 6 and 7 with $\nu_2 = 2.2 \text{ Hz}$ (see Fig. V-5) and for irradiation of line 1 with $\nu_2 = 5.25 \text{ Hz}$ (see Fig. V-7(a)). The value of C_{AB} given above is the final value chosen. Postponing the discussion on C_{AB} for the present, a comparison of the theoretical intensities for mechanism (i) with the observed values shows that $f(a)/f(B) = 2.0$ gives the best fit with the experiment.

Table V-2

Observed and calculated relative intensities for irradiation of lines 6 and 7 with an amplitude of 2.2 Hz and of line 1 with an amplitude of 5.25 Hz. The random field calculations are for $C_{B_1B_2} = 1.0$ and $C_{AB} = 0.0$. For irradiation of lines 6 and 7, the intensities are expressed relative to the intensity of line 3 (S.N. 5) as unity.

Irradia- tion at	S.N [†]	Observed relative intensity ‡‡	Calculated relative intensity ‡			
			Random field			Dipole- dipole
			f(A)/f(B)			
			1.5	2.0	2.5	
1	2	3	4	5	6	7
Line 6 v ₂ =2.2 Hz	1	0.33	0.31	0.30	0.29	0.28
	2	0.63	0.67	0.64	0.62	0.65
	3	0.42	0.44	0.42	0.40	0.40
	4	0.54	0.53	0.53	0.53	0.53
	5	1.00	1.00	1.00	1.00	1.00
	6	-	0.04	0.04	0.04	0.06
	7	0.46	0.44	0.44	0.44	0.45
	8	0.20	0.17	0.20	0.22	0.19
	9	0.28	0.26	0.30	0.33	0.29
	10	0.09	0.06	0.07	0.08	0.07
Line 7 v ₂ =2.2 Hz	1	0.23	0.11	0.12	0.14	0.11
	2	0.37	0.29	0.34	0.37	0.36
	3	0.22	0.17	0.20	0.22	0.15
	4	0.55	0.47	0.46	0.46	0.51
	5	1.00	1.00	1.00	1.00	1.00
	6	-	0.04	0.04	0.04	0.04

Table V-2(contd.)

	1	2	3	4	5	6	7
		7	0.55	0.49	0.50	0.50	0.51
		8	0.33	0.41	0.39	0.37	0.41
		9	0.50	0.47	0.45	0.43	0.50
		10	0.20	0.14	0.14	0.13	0.14
		1	-	0.02	0.02	0.02	0.02
		2	0.26	0.26	0.27	0.27	0.28
		3	1.03	1.03	1.03	1.03	0.92
Line 1		4	0.88	0.95	0.97	0.98	1.20
$\nu_2=5.25\text{Hz}$		5	0.78	0.66	0.63	0.62	0.65
		6	1.00	1.00	1.00	1.00	1.00
		7	0.25	0.16	0.16	0.16	0.23
		8	-	0.01	0.01	0.01	0.00

+ Serial number of the double resonance lines in a decreasing order of frequency (left to right in the spectrum).

†† These values are averages over several spectra (5-8) and are accurate approximately within 3 per cent of the values given.

‡ Calculated relative intensities have been obtained by dividing the calculated integrated intensities by observed linewidths.

The calculated intensities for $f(A)/f(B) = 1.5$ and 2.5 do not show striking deviations from the observed values. However, it may be noted, for example, for irradiation of line 6 with $\nu_2 = 2.2$ Hz (Table V-2), that the calculated intensities for $f(A)/f(B) = 1.5$ are consistently higher than the observed ones for lines 1, 2 and 3, and lower than the observed ones for lines 8, 9 and 10, while the opposite is true for $f(A)/f(B) = 2.5$. Such a feature is noticed for many different cases of irradiation. This leads to the conclusion that $f(A)/f(B) = 2.0$ gives the best fit. The values for mechanism (ii), however, also agree quite well with the experiment. Similar agreement is obtained for irradiation of these and other lines in the spectrum for various strengths of irradiation, so long as the strength of irradiation is large enough to satisfy Bloch approximation, indicating that the relative importance of these two mechanisms for this molecule cannot be distinguished on the basis of this calculation, which depends only on the relative values of the elements of the relaxation matrix.

The theoretical spectra for 'low' values of ν_2 , however, depend on the absolute values of the relaxation terms. The observed and calculated relative intensities for irradiation of lines 6 and 7 with $\nu_2 = 0.1$ Hz are given in Table (V-3). The calculated relative intensities for mechanism (i) are for $f(A)/f(B) = 2.0$, $C_{AB} = 0.0$ and three different values 0.1, 0.2 and 0.3 rad./sec. for $2f(B)\tau_c$.

Table V-3

Observed and calculated relative intensities (peak-heights) for weak irradiation of lines 6 and 7 with an amplitude $v_2 = 0.1$ Hz. The calculated intensities for random fields (mechanism (i)) are for $f(A)/f(B) = 2.0$, $C_{B1B2} = 1.0$ and $C_{AB} = 0.0$. All the intensities are expressed relative to the intensity of line 3 as unity.

Line	Transition	Single resonance intensity	Irradiation at line 6 (4→6)						Irradiation at line 7 (3→5)					
			Observed intensity†	Calculated intensity				Observed intensity†	Calculated intensity					
				Random fields		Dipole-dipole			Random fields		Dipole-dipole			
				2f(B)τ _c		τ _c in sec			2f(B)τ _c		τ _c in sec			
			0.10	0.20	0.30	5.0 x 10 ⁻¹⁰	2.7 x 10 ⁻¹¹		0.10	0.20	0.30	5.0 x 10 ⁻¹⁰	2.7 x 10 ⁻¹¹	
1	5 — 6	0.80	0.56	0.61	0.67	0.64	0.40	0.90	1.11	1.04	0.98	1.10	1.41	
2	3 — 4	0.98	1.22	1.17	1.12	1.18	1.57	0.80	0.73	0.79	0.84	0.74	0.35	
3	7 — 8	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
4	1 — 2	1.05	1.28	1.26	1.24	1.14	0.95	0.98	1.09	1.11	1.13	1.16	1.22	

† These values are averages of about five spectra and are accurate approximately within 5 per cent of the values given.

(this was the common factor not included in the calculation of relaxation matrix elements for spectra with large v_2) and those for mechanism (ii) are for $\tau_c = 5.0 \times 10^{-10}$ sec. and 2.7×10^{-11} sec.[†] From the trend of the relative intensities given for mechanism (i) and by making a similar comparison for irradiation of other lines, it was found that the spectra calculated with $2f(B)\tau_c = 0.2$ rad./sec. show consistently good agreement.

The results for mechanism (ii) with $\tau_c = 5.0 \times 10^{-10}$ sec. also agree well with the experiment. The correlation time appropriate for this mechanism is that for rotational diffusion, for which a hard sphere model for the rotation of the molecule gives:

$$\tau_c = \frac{4\pi\eta a^3}{3kT} \quad (V-1)$$

[†] These calculations were performed by assuming that only one off-diagonal element of χ , between the states connected by irradiation, is non-zero (see Sec. IIC-2(a)). However for irradiation of lines in 'B' group in which each line has a close neighbour, more than one off-diagonal element of χ could become significant. To estimate the effect of this a calculation in the rotating frame assuming two off-diagonal elements of $\tilde{\chi}$, between the states giving the close doublet (the doublet which is being irradiated), to be simultaneously significant was performed (see Sec. IIC-2(b)). This calculation leads to values of $\tilde{\chi}_{\alpha\alpha}$ which are not significantly different from those with only one off-diagonal element.

where η is the viscosity and ' a ' the hard sphere radius [7]. For the present sample $\eta \approx 1.0$ centipoise. At room temperature, the value of $\tau_c = 5.0 \times 10^{-10}$ sec. leads to a hard sphere radius of about 8.0 \AA . This value of ' a ' is considerably larger than the molecular dimensions. Furthermore, the natural linewidth of line 3, for example, given by $R_{\alpha\alpha'\alpha\alpha'}/\pi$ (full width at half height in Hz) becomes 0.65 Hz, for the above value of τ_c , which is larger than any of the observed linewidths, including the inhomogeneity, for single resonance transitions. On the other hand, if one assumes a value of ' a ' of the order of the molecular dimensions ($2 - 4 \text{ \AA}$), the calculated intensities (see Table V-3, for $\tau_c = 2.7 \times 10^{-11}$ sec. corresponding to ' a ' equal to 3.0 \AA) do not agree with the experiment. These considerations show that mechanism (ii) is not a dominant relaxation process for this molecule. It should, however, be noted that the above argument is based on the estimates of correlation time for the hard sphere model of rotational diffusion, and therefore the values given should be considered within the limitations of this model.

The effect of varying the correlation constant C_{AB} on the calculated spectrum for mechanism (i) is given in Table (V-4) along with the natural linewidths ($R_{\alpha\alpha'\alpha\alpha'}/\pi$) of the different transitions for different values of C_{AB} . Also shown in the Table (V-4) are the observed relative intensities and the sum of relaxation and instability widths, obtained by

Table V-4

Observed and calculated relative intensities (peak-heights) and linewidths of the double resonance transitions when line 6 is irradiated with an amplitude of 2.2 Hz. The calculated intensities and linewidths are for mechanism (i) having $C_{B_1B_2} = 1.0$, $f(A)/f(B) = 2.0$ and $2f(B)\tau_c = 0.2$ rad./sec.

S.N. [†]	Intensities				Linewidths [‡]				
	Observed	Calculated			Observed ^{††}		Calculated relax. width		
		C _{AB}					C _{AB}		
		1.0	0.5	0.0			1.0	0.5	0.0
Total	Relax.+ instab.								
1	0.33	0.29	0.30	0.30	0.65	0.29	0.35	0.31	0.27
2	0.63	0.61	0.63	0.64	0.78	0.42	0.35	0.30	0.25
3	0.42	0.40	0.41	0.42	0.83	0.47	0.34	0.29	0.24
4	0.54	0.52	0.52	0.53	0.54	0.36	0.24	0.25	0.25
5	1.00	1.00	1.00	1.00	0.60	0.42	0.13	0.13	0.13
6	-	0.04	0.04	0.04	-	-	0.24	0.25	0.25
7	0.46	0.44	0.44	0.44	0.62	0.44	0.26	0.26	0.25
8	0.20	0.20	0.20	0.20	0.50	0.50	0.15	0.19	0.24
9	0.28	0.29	0.29	0.30	0.42	0.42	0.17	0.21	0.25
10	0.09	0.07	0.07	0.07	-	-	0.19	0.23	0.27

[†] Serial numbers, as in Table (V-2).

[‡] Full linewidths at half height in Hz.

^{††} These values are averages over several spectra (5-8) and are accurate approximately within 5 per cent.

subtracting the inhomogeneity contribution from the observed widths. The intensities are not sufficiently sensitive to the value of C_{AB} , but the values of $R_{\alpha\alpha'\alpha\alpha'}$ depend on this constant quite considerably. It may be seen from the calculated values of $R_{\alpha\alpha'\alpha\alpha'}$, for $C_{AB} = 0.0, 0.5$ and 1.0 , that the effect of greater correlation between A and B is to introduce an asymmetry in the natural linewidths in the spectrum. The observed relaxation plus instability widths, however, do not show any systematic variations and since the instability is assumed to contribute ^{the} same width to all the transitions a comparison of the observed and calculated widths shows that C_{AB} is close to zero. This estimate is only approximate as it is coupled with the estimates of inhomogeneity contribution made from these linewidths. The effect of variation of $C_{B_1B_2}$ is shown in Table (V-5). This table shows that neither the calculated double resonance relative intensities nor the calculated linewidths are sufficiently sensitive to this parameter. However, as remarked earlier $C_{B_1B_2}$ has been taken as unity in the present case to maintain the complete equivalence of the two B protons. It may be noted that the values of correlation constants $C_{AB} = 0$ and $C_{B_1B_2} = 1.0$ have been finally deduced in this work by experimental evidence which is not striking enough to make a sharp distinction between the different values. The values given may, therefore, be considered to be indicative of the degree of correlation, rather than to signify an accurate estimate of the same.

Table V-5

Calculated relative intensities (peak-heights) and relaxation widths of the double resonance transitions when line 6 is irradiated by an amplitude of 2.2 Hz. These calculations are for mechanism (i) having $f(A)/f(B) = 2.0$, $C_{AB} = 0.0$, $2f(B)\tau_c = 0.2$ rad./sec. and different values of $C_{B_1B_2}$.

S.N.	Intensities			Linewidths		
	$C_{B_1B_2}$			$C_{B_1B_2}$		
	1.0	0.5	0.0	1.0	0.5	0.0
1	0.30	0.30	0.31	0.27	0.24	0.21
2	0.64	0.65	0.65	0.25	0.25	0.24
3	0.42	0.42	0.42	0.24	0.22	0.20
4	0.53	0.53	0.53	0.25	0.22	0.19
5	1.00	1.00	1.00	0.13	0.16	0.19
6	0.04	0.04	0.04	0.25	0.24	0.22
7	0.44	0.44	0.44	0.25	0.22	0.19
8	0.20	0.20	0.20	0.24	0.22	0.20
9	0.30	0.29	0.29	0.25	0.25	0.24
10	0.07	0.07	0.07	0.27	0.24	0.21

The theoretical values of $S_{\alpha\alpha}^+$ for the case of mechanism (i) having $f(A)/f(B) = 2.0$, $2f(B)\tau_c = 0.2$ rad./sec. $C_{AB} = 0.0$ and $C_{B_1B_2} = 1.0$ are plotted in juxtaposition with the double resonance spectra in Figs. (V-3) - (V-7). There is good agreement between the theoretical and experimental spectra in all the cases.

It should be pointed out that if the effect of magnetic field inhomogeneity is not properly taken into account the values of the relaxation parameters determined and the possible distinction between the theoretical calculations for different mechanisms would be completely altered and may lead to erroneous results. For example, in the present case, if the magnetic field inhomogeneity is assumed to contribute the same width to the different double resonance transitions, the value $f(A)/f(B)$ may have to be changed to nearly 4.0 and C_{AB} to 0.5 to fit the observed spectra.

It must be emphasized that it has been possible to conclude that mechanism (ii) is not an important relaxation process for the present case, only by combining the analyses of the results of double resonance spectra obtained for both strong and weak irradiation. The spectra for strong irradiation contain, in general, more information in the sense that there are more transitions for which a fit can be obtained, but the final fit in this case depends only on the relative values of the elements of the relaxation matrix. The spectra for weak irradiation, on the other hand, contain

fewer parameters to obtain a fit, but the calculation depends on the absolute values of the elements of the relaxation matrix. This is an interesting distinction between these two categories of spectra and can be used with considerable advantage in the study of relaxation by double resonance methods.

This analysis leads to the conclusion that the random isotropic fields at the site of nucleus A have a mean square value twice that at the sites of B nuclei. This excludes the other spins in the molecule as important sources of these random fields as nucleus A is farther off than the B nuclei from the remaining spins in the molecule. The proton relaxation thus appears to be caused primarily by intermolecular dipolar interactions. Since the sample is a 20 per cent solution by weight in CCl_4 (which is nearly a saturated solution) each molecule of 2,6-dibromoaniline is, on an average, surrounded much more by CCl_4 molecules than the molecules of the same kind (a 20 per cent solution by weight of 2,6-dibromoaniline in CCl_4 has approximately seven CCl_4 molecules per one 2,6-dibromoaniline molecule). It was not feasible to look for a possible concentration dependence of this relaxation since the range in which the concentration could be reduced, without seriously affecting the signal to noise ratio, would slightly increase the number of CCl_4 molecules and would not significantly alter the physical situation in the immediate vicinity of a dibromoaniline molecule.

Chapter VI

DOUBLE RESONANCE STUDY OF PROTON RELAXATION IN A TWO
SPIN SYSTEM (AB) COUPLED TO A QUADRUPOLEAR NUCLEUS

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VI - DOUBLE RESONANCE STUDY OF PROTON RELAXATION IN A TWO
SPIN SYSTEM (AB) COUPLED TO A QUADRUPOLEAR NUCLEUS

VIA INTRODUCTION

In this chapter the results of a proton-proton double resonance study of relaxation in a two spin system (AB), the spectra of which exhibit broadening due to coupling with a neighbouring N^{14} nucleus, are presented. The AB system is formed by the protons in 2-bromothiazole which is studied in the form of a neat liquid. The scalar coupling of the protons with the N^{14} nucleus modulated by the rapid quadrupolar relaxation of the latter is an important source of proton relaxation in this molecule. The analysis of double resonance experiments performed by irradiating each of the single resonance transitions for different strengths of irradiation led to some detailed information on the scalar coupling interaction viz. the magnitudes and relative sign of proton- N^{14} coupling constants, as well as the parameters describing the other mechanisms of relaxation in this molecule, in particular internal dipole-dipole interaction. Conventional relaxation time and linewidth measurements were also used to facilitate the double resonance analysis. It was shown by this study that, in general, it is possible through relaxation studies by double resonance, to obtain the relative sign of the coupling constants of protons with quadrupolar nucleus. The spectra for 'low' strengths of irradiation were analysed by the graphical method, mentioned in Sec. IIIC.

VIB RELATIVE SIGN OF SCALAR COUPLING CONSTANTS

When there is more than one spin coupled to a quadrupolar nucleus, the relaxation matrix elements for the spin system contain terms arising from cross-products between various scalar coupling interactions. These interactions are completely correlated because the time-dependence is caused by the same quadrupolar nucleus and these cross-terms do not therefore vanish. For two spins both of which are coupled to the same quadrupolar nucleus the scalar coupling interaction may be written as (see Eq. III-10),

$$\mathcal{H}_{sc}(t) = 2\pi(J_{AN} \underline{I}(A) + J_{BN} \underline{I}(B)) \cdot \underline{S}_N(t) \quad (\text{VI-1})$$

The spectral densities (Eq. II-30) will then contain terms of the type:

$$4\pi^2 \left\langle \alpha \left| (J_{AN} \underline{I}(A) + J_{BN} \underline{I}(B)) \cdot \underline{S}_N(t) \right| \beta \right\rangle \left\langle \alpha' \left| (J_{AN} \underline{I}(A) + J_{BN} \underline{I}(B)) \cdot \underline{S}_N(t-\tau) \right| \beta' \right\rangle \quad (\text{VI-2})$$

which depend, in general, on the relative sign of J_{AN} and J_{BN} . This suggests the possibility of determination of these relative signs by studying the relaxation matrix elements.

These relaxation matrix elements depend on the relative sign of J_{AN} and J_{BN} even in the case of single resonance. In single resonance spectra these matrix elements determine the

linewidths of the different transitions. However, in cases in which $4\pi^2 J^2 \ll (\omega_I - \omega_S)^2$ and $(\omega_I - \omega_S)^2 \tau_q^2 \gg 1$ the relaxation is contributed only by the terms $2\pi[J_{AN}I_Z(A) + J_{BN}I_Z(B)]S_N^Z(t)$ of Eq. (VI-1) (see Sec. IIIC) and the widths of each of the transitions belonging in the zeroth order, to 'A' nucleus is $4\pi^2(J_{AN}^2 \cos^2 \theta + J_{BN}^2 \sin^2 \theta)$ and to the 'B' nucleus is $4\pi^2(J_{BN}^2 \cos^2 \theta + J_{AN}^2 \sin^2 \theta)$ where $\tan \theta = J_{AB}/(\nu_A - \nu_B)$. The single resonance spectra in such cases do not, therefore, depend on the relative sign of J_{AN} and J_{BN} .

The double resonance spectra, however, depend on a variety of relaxation matrix elements and are therefore expected to depend on the relative signs through the intensities as well as linewidths of various transitions. This fact has been utilized in the present case to find the relative sign of J_{AN} and J_{BN} .

VIC EXPERIMENTAL RESULTS

1. Single Resonance Spectrum

The single resonance proton spectrum of 2-bromothiazole is shown in Fig. (IV-5). This is a typical four line AB spectrum, having additional broadening due to scalar coupling of the protons with nitrogen. The low field ('A' proton) doublet is assigned to the proton in position 4. This proton being nearer to nitrogen compared to the proton in position 5 ('B' proton) will couple strongly with it, giving a broader doublet. This assignment is same as that in [44].

The spectral analysis of an AB spin system is straight forward [2]. The analysis gives the values of the coupling constant $J_{AB} = 3.55 \pm 0.05$ Hz and the chemical shift $|\nu_A - \nu_B| = 18.8 \pm 0.1$ Hz between the two protons.

2. T_1 and T_2 Measurements

Measurements of spin-lattice relaxation time T_1 and spin-spin relaxation time T_2 were made in order to derive some information on the magnitudes of scalar coupling of the protons with N^{14} . The magnetic field was made sufficiently inhomogeneous for the doublet of each proton to collapse into a broad line and T_1 and T_2 for each such doublets were measured. T_1 was measured by the ~~adiabatic~~ rapid passage method [45]. The result of one such experiment is shown in Fig. (VI-1) and a plot between $\log (M_0 - M_z)$ and time 't' in Fig. (VI-2). The slope of this straight line is a measure of T_1 . The values of T_1 obtained by this method for the 'A' proton (low field broad doublet) and the 'B' proton (high field sharp doublet) are 9.1 ± 0.5 sec. and 8.8 ± 0.5 sec. respectively..

The spin-spin relaxation time T_2 was measured for the 'B' proton by adiabatic rapid passage into the center of a u-mode resonance with a large r.f. field (large compared to the inhomogeneity of the magnetic field), stopping the sweep at that point and monitoring the rate of decay [45]. This decay is exponential with a time constant T_2 and a typical curve obtained for the 'B' doublet is shown in Fig. (VI-3),

Fig. VI-1. Recovery curve for the adiabatic rapid passage method of T_1 measurement for the high field doublet of 2-bromothiazole. The successive peaks are one second apart.

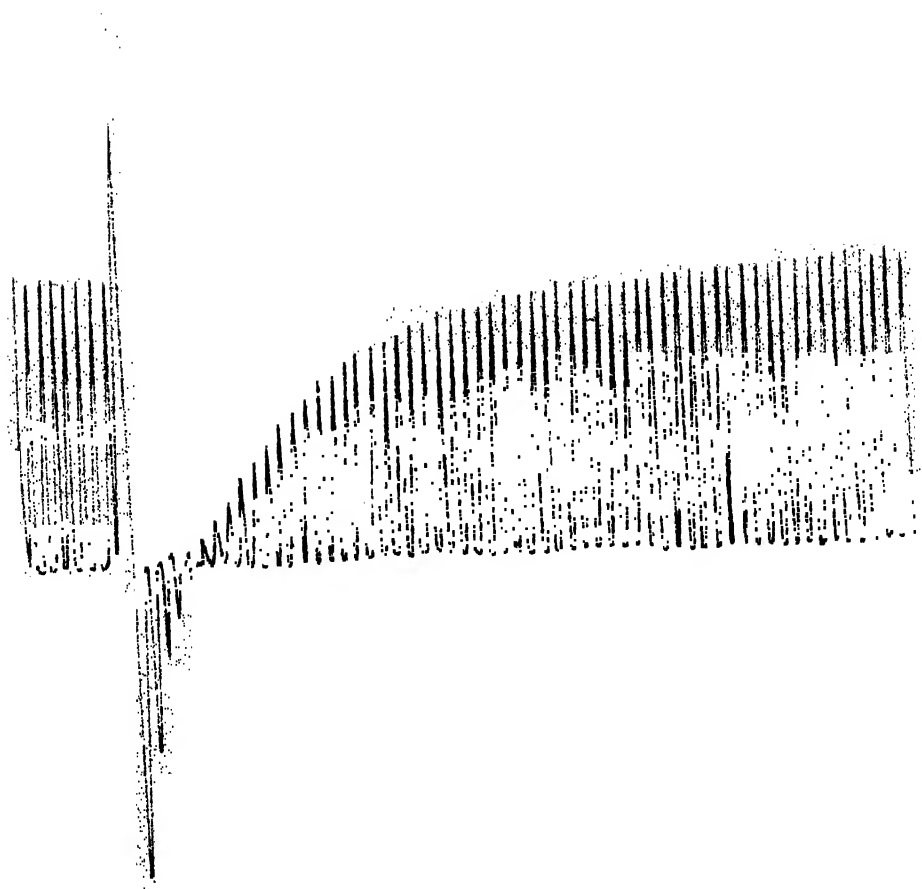


Fig. VI-2. $\text{Log}(M_0 - M_z)$ versus time (t) graph for T_1 measurement of high field doublet of 2-bromothiazole.

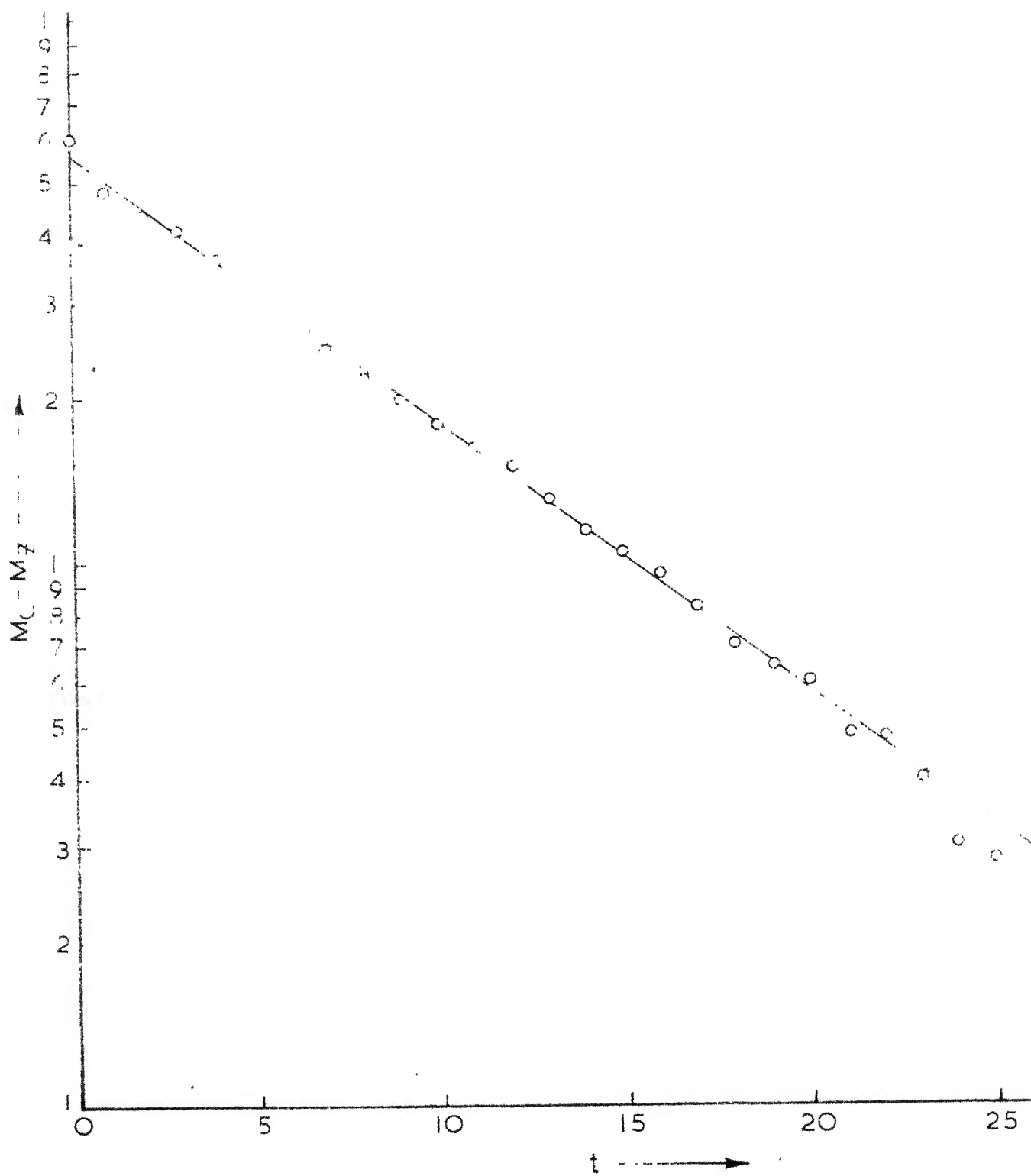
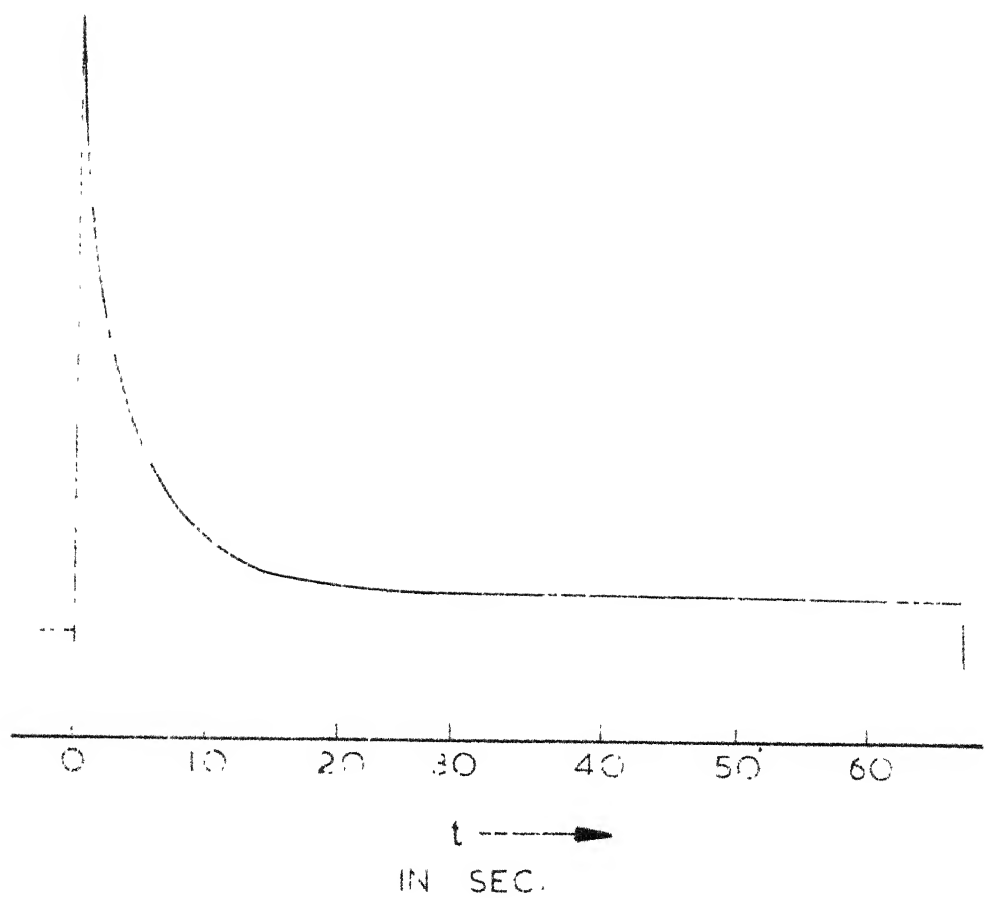


Fig. VI-3. Saturation curve for the adiabatic rapid passage method of T_2 measurement for the high field doublet of 2-bromothiazole.



from which a value of T_2 is obtained as 3.6 ± 0.2 sec. The value of T_2 for the 'A' proton is comparatively very small due to its stronger coupling with N^{14} and therefore could not be measured by this experiment.

Nitrogen (N^{14}) resonance was observed on a Varian V-4200 wideline n.n.r. spectrometer, operating at 2.695 MHz (field ~ 8.76 K.G.), using audio sweep modulation. Modulation frequency of 20 Hz and sweep amplitude of 1.0 gauss were used. The spectrum was observed in the v-mode and the peak-to-peak linewidth of the first derivative, after applying a modulation correction [46], was obtained as 0.98 gauss, which gives a fullwidth at half height of a lorentzian as 1.70 gauss. This leads to the relaxation time τ_q ($T_1 = T_2 = \tau_q$) for N^{14} as 0.61 millisecc.

3. Double Resonance

Some of the typical double resonance spectra obtained are shown in Figs. (VI-4)-(VI-6). The calibration for the strengths of irradiation was done in the manner described in Sec. VC. Figure (VI-4) shows the irradiation of each one of the single resonance lines by an amplitude of 0.135 Hz. 'Low' irradiation amplitude spectra have been obtained for two more strengths viz. 0.076 and 0.043 Hz, for irradiation of each of these lines. These spectra show significant intensity changes in the spectrum of the proton other than the one being irradiated. These changes are large for transitions having energy levels in common with the pair being

Fig. VI-4. Frequency sweep double resonance spectra of 2-bromothiazole, for "low" strengths of irradiation, obtained by irradiating (a) inner line of proton A, (line 3), (b) outer line of proton A, (line 4), (c) inner line of proton B, (line 2) and (d) outer line of proton B, (line 1). The strength of irradiation in each case is 0.135 Hz.



Fig. VI-5. Observed and calculated double resonance spectra for irradiation of (a) outer line of proton A (line 4) and (b) inner line of proton A (line 3) in 2-bromothiazole, with amplitude of irradiation 2.4 Hz. The calculated spectra are for internal dipole-dipole interaction and scalar coupling (mechanism (i)) with $K = 4.0$ and $J_{BN}/J_{AN} = 0.3$.

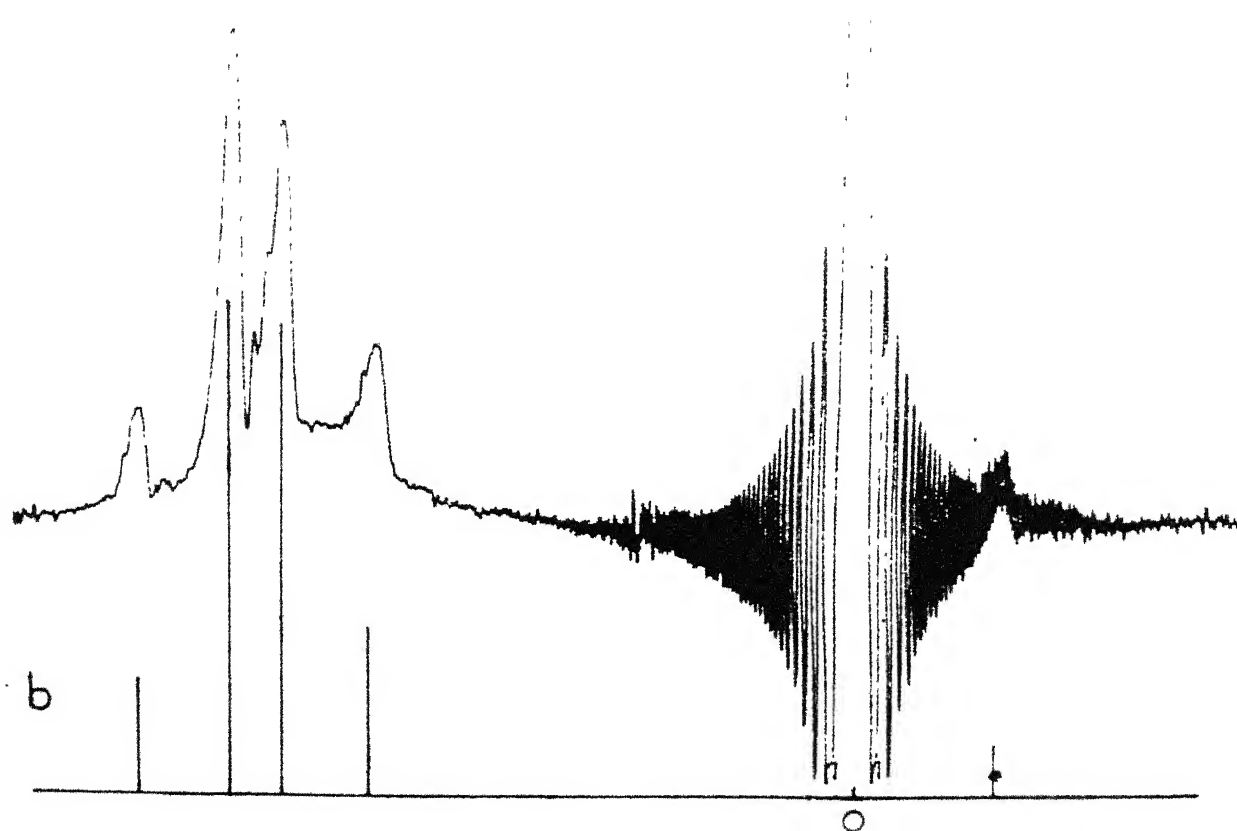
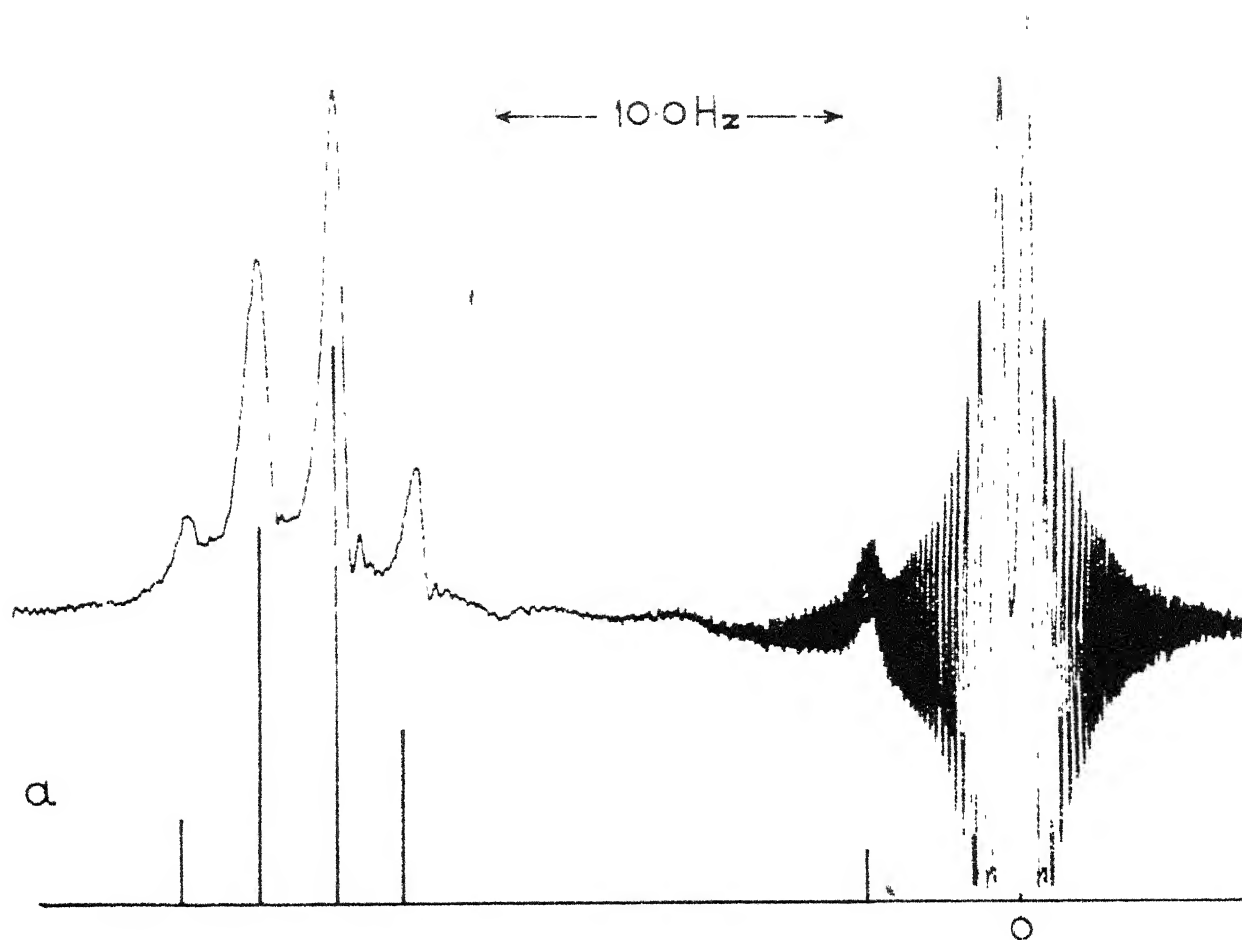
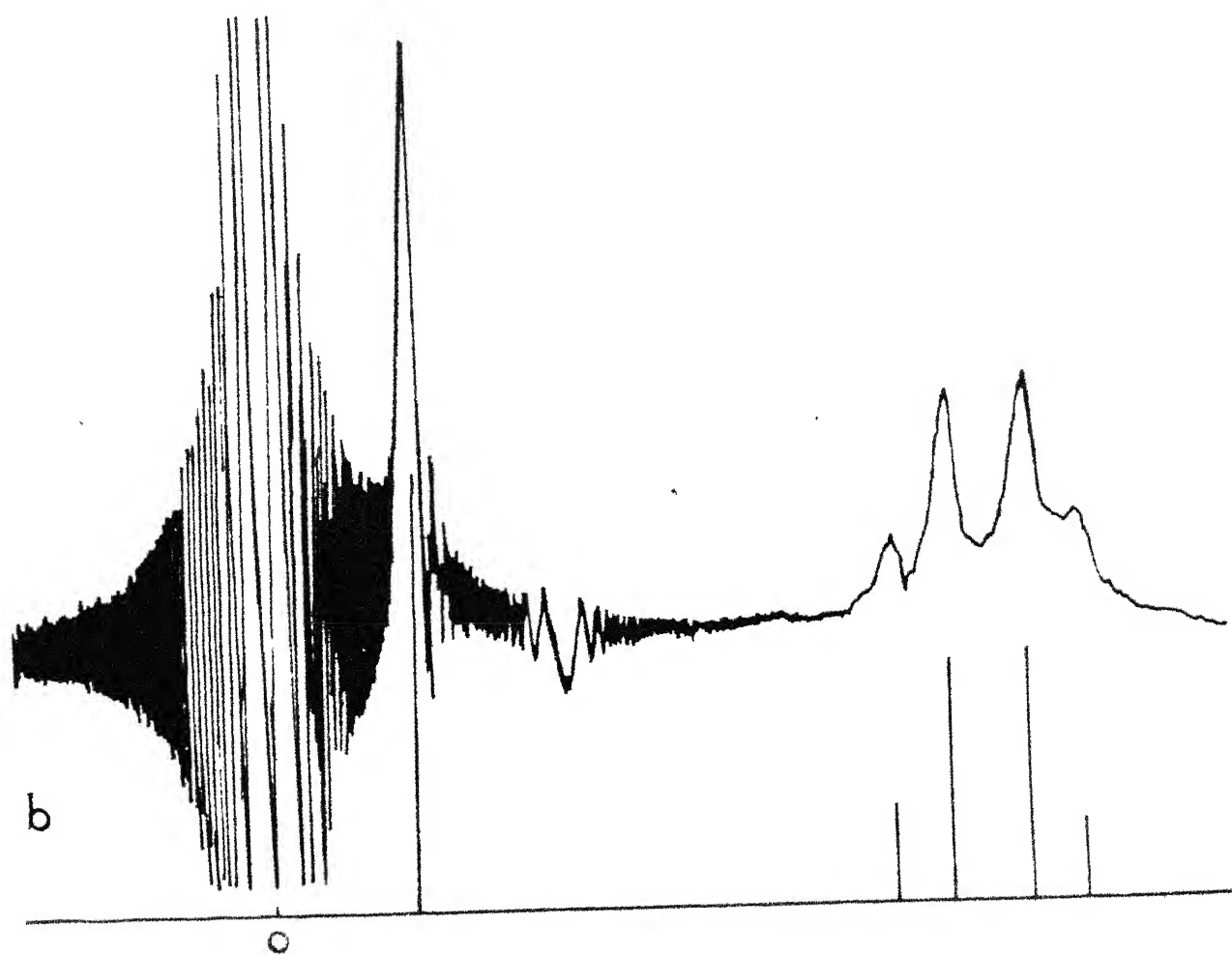
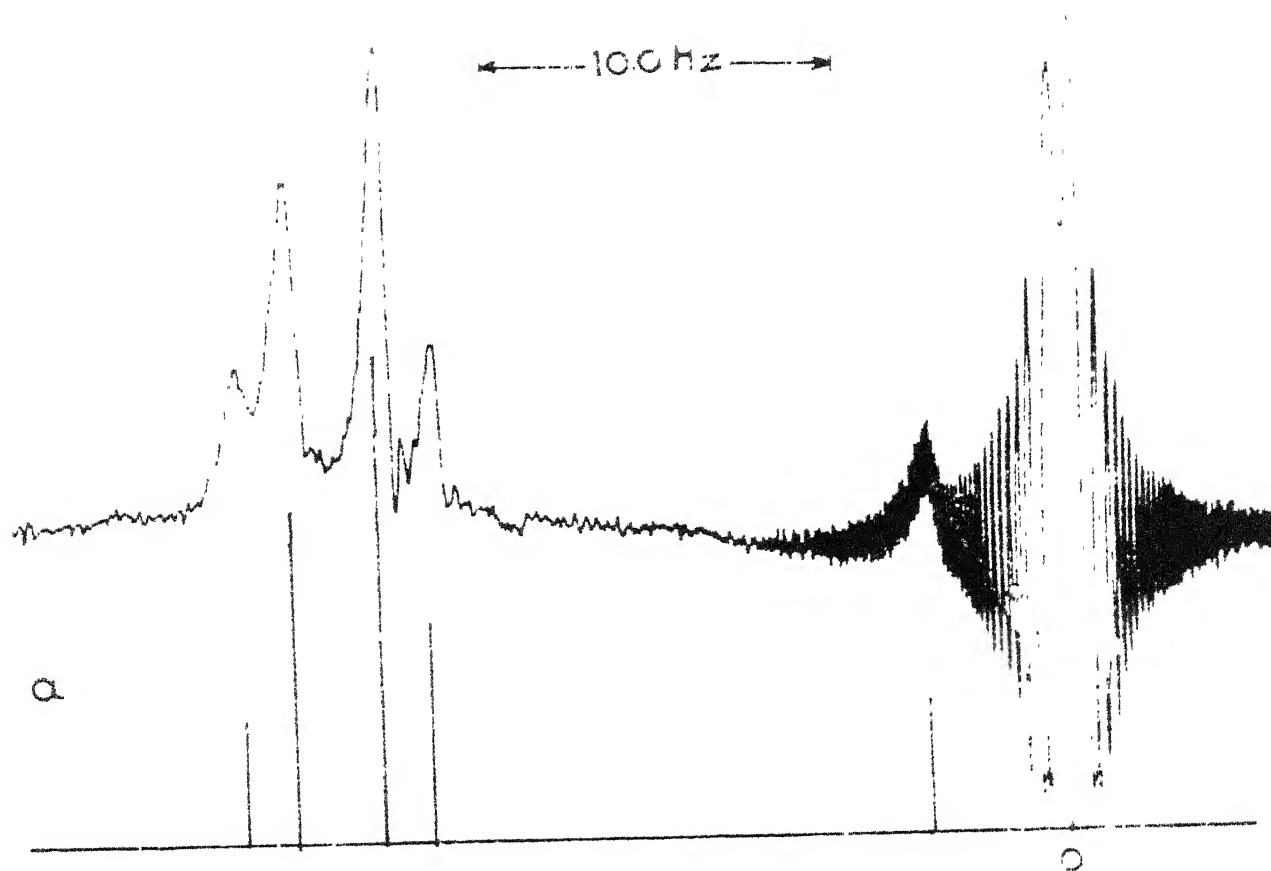


Fig. VI-6. Observed and calculated double resonance spectra of 2-bromothiazole for irradiation of (a) outer line of proton A (line 4) with strength of irradiation 1.6 Hz and (b) outer line of proton B (line 1) with strength of irradiation 1.75 Hz. The calculated spectra are for internal dipole-dipole interaction and scalar coupling (mechanism (i)) with $K = 4.0$ and $J_{BN}/J_{AN} = 0.3$.



irradiated and can be qualitatively understood on the basis of arguments, using an energy level diagram, similar to the ones described earlier (Sec. VC-1). The spectra with 'high' strengths of irradiation show all the features of a double resonance spectrum (Figs. VI-5,6). The contribution to the linewidths to these double resonance transitions is also, in general, different for different transitions. Reliable estimates of this contribution for different transitions are obtained by using the plots of $\omega_{\alpha\alpha}/2\pi$ versus A_j . These estimates are, however, approximate since the spin system, in the present case, is not weakly coupled.

VID ANALYSIS

1. Estimates of Scalar Coupling Strengths

The contribution of either dipole-dipole interaction or external random fields to T_1 and T_2 , for very short correlation times, are equal (extreme narrowing), while this is usually not the case for the scalar coupling mechanism, since the corresponding correlation time is rather long, in comparison [7]. Therefore, wherever scalar coupling contributes to relaxation, a difference between the values of T_1 and T_2 gives information on the extent of this coupling. Estimates of coupling constants J_{AN} and J_{BN} of protons A and B respectively with N^{14} may then be obtained by using Eqs. (III-49,50) and an assumption that the relaxation matrix element of the type $R_{\alpha\beta\alpha\beta}$ represents $(-1/T_2)_A$, where $\alpha \rightarrow \beta$

is a 'A' transition in the zeroth order[†]. This leads, for a coupled spin system AB under the assumption that only terms of the type $I_z S_z$ of $\mathcal{H}_{sc}(t)$ in Eq. (VI-1) are significant, to:

$$\left(\frac{1}{T_2} - \frac{1}{T_1}\right)_B = \left[\left(\frac{1}{T_2}\right)_{sc}\right]_B = \frac{4\pi^2 S(S+1)}{3} \tau_q (J_{AN}^2 \sin^2 \theta + J_{BN}^2 \cos^2 \theta) \quad (\text{VI-3})$$

and

$$\begin{aligned} \left(\frac{1}{T_2}\right)_A - \left(\frac{1}{T_2}\right)_B &= \left[\left(\frac{1}{T_2}\right)_{sc}\right]_A - \left[\left(\frac{1}{T_2}\right)_{sc}\right]_B \\ &= \frac{4\pi^2 S(S+1)}{3} \tau_q (J_{AN}^2 - J_{BN}^2) \cos 2\theta, \quad (\text{VI-4}) \end{aligned}$$

where the subscripts 'A' and 'B' refer to the two protons and the subscript 'sc' to scalar coupling. Equation (VI-4) gives the difference between the observed single resonance linewidths of A and B protons, if the contribution to these linewidths from other sources (namely, inhomogeneity of the magnetic field and other mechanisms of relaxation) is assumed to be the same.

† It may be noted that it is, in principle, possible to derive the values of the scalar coupling constants by double resonance data alone. However, estimates made on the basis of approximate determinations of T_1 and T_2 serve as a useful starting point for obtaining fit with the double resonance experiments, and would facilitate the determination of the parameters of the other mechanisms.

Using the experimentally determined values of $(T_1)_B$ and $(T_2)_B$ respectively 8.8 sec. and 3.6 sec. and $\tau_q = 0.61$ millisecc, in Eq. (VI-3), and equating the observed linewidth difference between the A and B proton resonances (≈ 0.35 Hz) to Eq. (VI-4), gives: $J_{AN} = 8.8$ Hz and $J_{BN} = 3.1$ Hz. This value of J_{AN} compares favourably with a similar estimate of 10.8 Hz by Kintzinger and Lehn for thiazole [37].

For these values of J_{AN} and J_{BN} and the observed τ_q , the condition mentioned in Sec. IIIC, for complete washing out of the scalar coupling ($\eta^2 \ll 1$) is satisfied. Therefore, for the present sample the treatment of scalar coupling only as a mechanism for relaxation is valid.

2. Other Details

The proton-proton distance in this molecule enters the internal dipole-dipole interaction calculation. Information is available on bond angles and bond lengths in thiazole, through studies of C^{13} - H^1 coupling constants [47]. Assuming that the bromine substitution does not significantly alter the geometry of the molecule, the distance between the two protons in 2-bromothiazole is obtained as 1.66 Å.

Theoretical single and double resonance spectra have been calculated by considering (i) internal dipole-dipole interaction and scalar coupling and (ii) external isotropic random fields and scalar coupling as possible alternative mechanisms for relaxation. For double resonance spectra with

'high' strengths of irradiation, for which $|\gamma_{H_2}| \gg |\Gamma_{\alpha\alpha'}|$, Bloch approximation has been used (see Sec. IIC). Since under Bloch approximation the calculated spectra depend only on the relative value of the relaxation matrix elements, these spectra have been calculated by varying a parameter K , which determines the relative contribution of dipole-dipole and scalar coupling in mechanism (i) and random field and scalar coupling in mechanism (ii). For random fields, however, there are two more parameters namely the ratio of mean square fields $f(A)/f(B)$ at the sites of the two protons and C the correlation constant between these fields. The ratio $f(A)/f(B)$ was varied in the calculations to obtain a fit with experiment, but C was fixed from the information available from the observed single resonance linewidths. The observed single resonance linewidths are more for the two inner lines in the AB quartet, in this case, than the outer lines, indicating that C is close to unity [ref. 7, p. 509], and was taken to be 1. It may further be remarked in this connection that while the internal dipole-dipole also contributes greater widths to the inner lines compared to outer ones, in the AB quartet, the scalar coupling contributes equal widths to the two lines of a proton resonance in it.

For the double resonance spectra with "low" strengths of irradiation, the observed and calculated straight line plots (Eq. II-80) were drawn and compared.

VIE DISCUSSION

Table (VI-1) shows the observed and calculated double resonance peak heights, the observed single and double resonance linewidths and calculated single and double resonance relaxation widths for irradiation of outer line of 'A' resonance by amplitudes of irradiation $\nu_2 = 1.6$ and 2.4 Hz and for irradiation of outer line of 'B' resonance by an amplitude $\nu_2 = 1.75$ Hz. A satisfactory fit for observed peak heights and linewidths is obtained for mechanism (i) for $K = 4.0$ and $J_{BN}/J_{AN} = 0.3$ and for mechanism (ii) for $K = 4.0$, $J_{BN}/J_{AN} = 0.3$ and $f(A)/f(B) = 0.5$. The parameter K is equal to $[(16\pi^2 J_{AN}^2 \tau_q / 3) / (\gamma^4 h^2 \tau_c / r^6)]^{1/2}$ for mechanism (i) and equal to $[(16\pi^2 J_{AN}^2 \tau_q / 3) / (2f(B) \tau_c)]^{1/2}$ for mechanism (ii). A variation in J_{BN}/J_{AN}^\dagger does not seriously affect the calculated peak heights, but alters the calculated linewidths. The $\omega_{\alpha\alpha'}/2\pi$ versus A_j plots for approximate estimation of inhomogeneity contribution to various double resonance transitions were drawn and one such plot for irradiation of 'A' proton by $\nu_2 = 2.4$ Hz is shown in Fig. (VI-7). This plot indicates, for irradiation of the outer line of 'A' resonance which corresponds to $A_A = -1.94$ Hz, approximately 40 per cent increase in the recoverable part of single resonance inhomogeneity contribution (the instability contribution is not recoverable)

[†] Though this quantity has been estimated from T_1 and T_2 measurements, the accuracy of these measurements is limited in as much as these measurements were made for overlapping doublets.

Table VI-1

Observed and calculated relative intensities (peak-heights)[†] and linewidths[†] for irradiation of outer line of 'A' proton (line 4) by amplitudes 2.4 Hz and 1.6 Hz and of outer line of 'B' proton (line 1) by an amplitude of 1.75 Hz.

Line	Observed	Dipole-dipole + scalar coupling										Random field + scalar coupling	
		$J_{BN}/J_{AN} = 0.3$										$K=4.0; J_{BN}/J_{AN}=0.3$	
		1	2	3	4	5	6	7	8	9	10	1.0	0.5
Single resonance	Line width	1	0.55	0.08	0.10	0.13	0.07	0.13	0.10	0.13	0.10	0.13	0.12
		2	0.58	0.08	0.10	0.14	0.08	0.14	0.10	0.14	0.10	0.14	0.13
		3	0.92	0.51	0.54	0.58	0.54	0.54	0.54	0.54	0.54	0.58	0.55
		4	0.88	0.51	0.53	0.56	0.53	0.53	0.53	0.53	0.53	0.57	0.54
Intensity		1	0.17	0.13	0.14	0.15	0.14	0.14	0.15	0.14	0.15	0.15	0.14
		2	0.67	0.66	0.68	0.73	0.69	0.68	0.71	0.68	0.71	0.74	0.67
		3	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00

Table VI-1 (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
Double resonance		4	0.28	0.32	0.31	0.30	0.31	0.31	0.31	0.31	0.31	0.31
		5	0.17	0.10	0.13	0.17	0.13	0.14	0.18	0.20	0.13	0.07
irradia- tion of line 4	Line- width	1	0.89	0.44	0.46	0.49	0.39	0.53	0.22	0.55	0.51	0.49
		2	0.89	0.43	0.45	0.49	0.39	0.52	0.22	0.52	0.49	0.48
		3	0.66	0.20	0.21	0.25	0.23	0.21	0.44	0.25	0.24	0.23
$v_2=2.4$ Hz		4	0.67	0.19	0.21	0.23	0.22	0.20	0.44	0.26	0.24	0.23
		5	1.00	0.43	0.45	0.49	0.45	0.45	0.45	0.50	0.46	0.44
Double resonance	Inten sity	1	0.32	0.24	0.26	0.27	0.26	0.26	0.28	0.27	0.25	0.23
		2	0.70	0.65	0.69	0.75	0.70	0.63	0.76	0.74	0.66	0.60
		3	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
		4	0.39	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
irradia- tion of line 4		5	0.17	0.22	0.28	0.39	0.30	0.27	0.41	0.39	0.25	0.14
$v_2=1.6$ Hz	Line- width	1	0.89	0.45	0.47	0.51	0.40	0.55	0.21	0.56	0.53	0.50
		2	0.98	0.45	0.47	0.51	0.40	0.54	0.21	0.54	0.51	0.49
		3	0.67	0.18	0.20	0.23	0.22	0.19	0.45	0.23	0.22	0.21
		4	0.67	0.18	0.19	0.22	0.21	0.18	0.45	0.24	0.22	0.21
		5	1.00	0.47	0.49	0.53	0.49	0.49	0.49	0.54	0.50	0.48

Table VI-1 (Contd.)

1	2	3	4	5	6	7	8	9	10	11	12	13
		1	2.21	1.74	1.75	1.76	1.94	1.56	2.14	1.72	1.92	2.27
	Inten	2	0.35	0.37	0.37	0.37	0.33	0.41	0.29	0.38	0.33	0.26
	sity	3	0.96	1.00	0.96	0.91	0.86	1.07	0.79	1.13	0.98	0.77
Double		4	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
resonance		5	0.45	0.32	0.32	0.31	0.32	0.31	0.32	0.34	0.33	0.33
irradia-												
tion of		1	0.62	0.08	0.10	0.14	0.08	0.13	0.10	0.14	0.12	0.11
line 1		2	0.97	0.39	0.41	0.44	0.44	0.38	0.66	0.45	0.43	0.42
$\nu_2=1.75\text{Hz}$	Line-	3	0.89	0.40	0.42	0.45	0.45	0.39	0.67	0.45	0.43	0.42
	width	4	1.30	0.65	0.68	0.71	0.62	0.73	0.43	0.75	0.71	0.68
		5	1.27	0.66	0.69	0.72	0.63	0.74	0.42	0.77	0.74	0.71

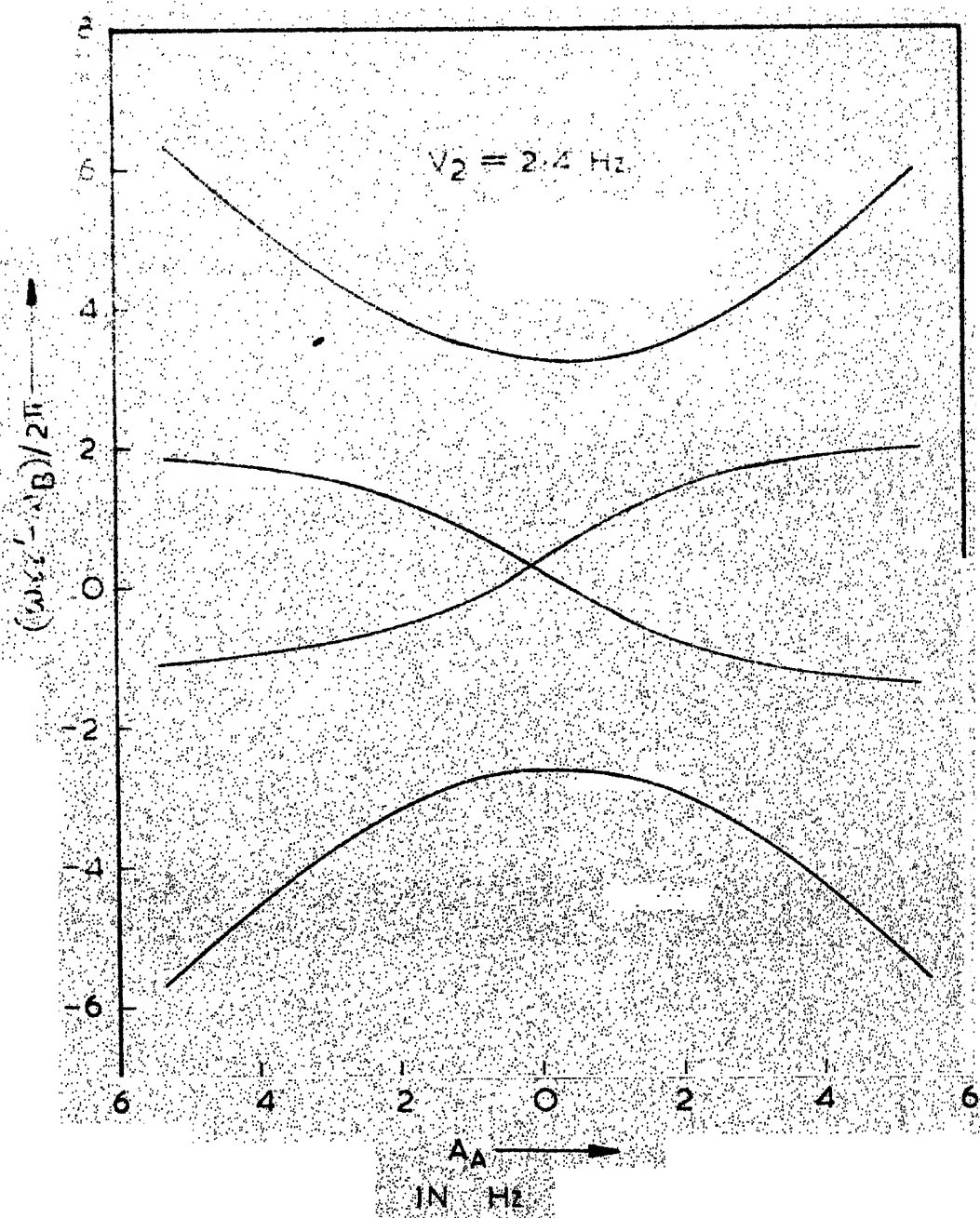
All measurements are averages over several spectra (≥ 5). The intensities are accurate within 5 per cent and the linewidths within 10 per cent of the values given.

+ Calculated relative intensities have been obtained by dividing the calculated integrated intensities by observed linewidths.

† Full linewidths at half height in Hz. This table contains calculated relaxation widths and observed full widths.

++ Lines are numbered in the increasing order of frequency (left to right in the spectrum).

Fig. VI-7. Plots of calculated double resonance frequencies of 'B' transitions versus "frequency-offset" of irradiation of 'A' nuclei. These plots are calculated for the AB spin system for $\nu_2 = 2.4$ Hz. Irradiation of line 1,2,3 and 4 correspond respectively to $A_A = 20.74$, 17.19 , 1.61 and -1.94 Hz.



for lines 1 and 2 of the double resonance spectrum and a corresponding decrease in lines 3 and 4. If the recoverable part of the inhomogeneity is assumed to contribute a full-width at half height ~ 0.15 Hz to single resonance transitions (see Sec. VC-2), the observed and calculated single and double resonance widths fit best for $J_{BN}/J_{AN} = 0.3$. A detailed comparison of the double resonance spectra obtained for different frequencies and amplitudes of irradiation ~~been made~~ and led to a satisfactory fit for the above mentioned parameters for mechanisms (i) and (ii).

The effect of a change of sign of J_{BN} with respect to J_{AN} is also shown in Table (VI-1). The single resonance linewidths are not changed as shown in Sec. (VIB). However, the double resonance linewidths show a marked difference between the two alternative cases of same sign and opposite sign. The linewidths for the case of opposite sign are widely different from the observed ones, leading to a conclusion that both J_{AN} and J_{BN} are of the same sign.

The spectra for 'low' amplitudes of irradiation have been calculated for the above two mechanisms with parameters K and J_{BN}/J_{AN} same as ^{those} ~~^~~ which led to a satisfactory fit for 'high' amplitude of irradiation case, and by varying the absolute values of the relaxation matrix elements. This amounts to, for a given value of τ_q , a simultaneous variation in τ_c , J_{AN} and J_{BN} for mechanism (i) and in $2f(B)\tau_c$, J_{AN} and J_{BN} for mechanism (ii) such that K and J_{BN}/J_{AN} are unchanged. A fit for 'low' and 'high' amplitude of irradiation spectra

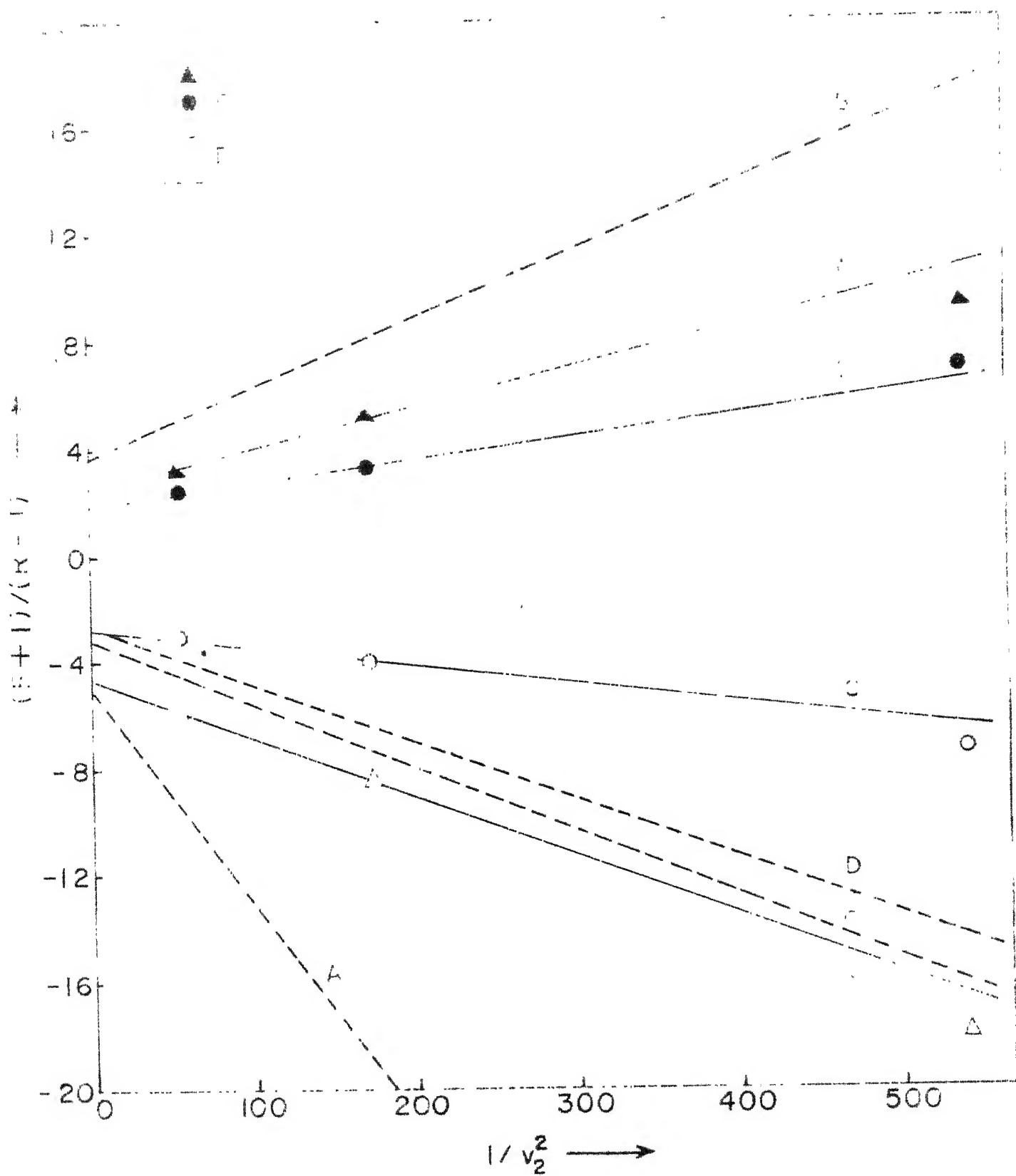
then determines the values of these parameters as obtained by double resonance analysis. However, some information on J_{AN} and J_{BN} is available from relaxation time measurements and therefore the absolute values of the relaxation matrix elements need be varied only over a small range. Table (VI-2) gives the observed and calculated values of R , Eq. (II-79), for various transitions in the double resonance spectra for 'low' irradiation of A group of lines. The calculated values are for $K = 4.0$; $J_{BN}/J_{AN} = 0.3$ and different absolute values of relaxation matrix elements. A satisfactory fit with the observed values of R is obtained for mechanism (i) with $\tau_c = 7.0 \times 10^{-12}$ sec. For mechanism (ii) no satisfactory fit is obtained. Also shown in Fig. (VI-8) are the plots of observed and calculated ratios $(R+1)/(R-1)$ between various transitions versus $1/(v_2^2)$, for irradiation of the 'A' group of lines with 'low' amplitudes of irradiation (see Eq. II-80). While the observed ratios are indicated by various points on the graph, the calculated ratios are shown by straight lines. The fit between the observed points and the calculated ratios for mechanism (i) (continuous lines), for $K = 4.0$, $J_{BN}/J_{AN} = 0.3$ and $\tau_c = 7.0 \times 10^{-12}$ sec. is satisfactory. These parameters give $J_{AN} \approx 9.7$ Hz and $J_{BN} \approx 2.9$ Hz for $\tau_q = 0.61$ millisecc. For mechanism (ii), however, no satisfactory fit could be obtained for any plausible values of the parameters, and the plots in Fig. (VI-8) for this mechanism (broken lines), for $K = 4.0$; $J_{BN}/J_{AN} = 0.3$ and $2f(B)\tau_c = 0.19$ rad./sec.

Table VI-2

The observed and calculated values of R (see Eq. II-79) for "low" irradiation of 'A' group of lines. The calculated values for both mechanisms (i) and (ii) are for $K = 4.0$ and $J_{BN}/J_{AN} = 0.3$. For mechanism (ii) the additional parameters are $f(A)/f(B) = 0.5$ and $C = 1.0$.

Irrad- iation at	ν_2 in Hz	Ratio of lines	Observed	mechanism (i)			mechanism (ii)		
				$\tau_c \times 10^{-12}$ sec			$2f(B)\tau_c$		
				11.0	7.0	4.7	0.29	0.19	0.13
Line 4	0.043	2/1	0.76	0.88	0.77	0.64	0.94	0.89	0.81
		3/1	0.89	0.94	0.88	0.82	0.93	0.87	0.77
	0.076	2/1	0.61	0.72	0.59	0.48	0.86	0.76	0.68
		3/1	0.79	0.86	0.79	0.73	0.83	0.73	0.63
	0.135	2/1	0.50	0.54	0.45	0.40	0.73	0.64	0.59
		3/1	0.71	0.76	0.71	0.69	0.69	0.59	0.53
Line 3	0.043	2/1	1.33	1.18	1.36	1.67	1.06	1.12	1.23
		4/1	1.24	1.10	1.20	1.38	0.98	0.96	0.92
	0.076	2/1	1.89	1.47	1.84	2.30	1.16	1.28	1.43
		4/1	1.48	1.27	1.48	1.74	0.94	0.90	0.84
	0.135	2/1	2.54	2.04	2.50	2.88	1.33	1.48	1.60
		4/1	1.89	1.59	1.86	2.07	0.88	0.81	0.78

Fig. VI-8. Plots of observed and calculated ratios $(R+1)/(R-1)$ versus $1/v_2^2$ for 'low' strengths of irradiation, for 2-bromothiazole. The points indicate the observed ratios and the straight lines the theoretical ratios. The solid lines are for mechanism (i) with $K = 4.0$, $J_{BN}/J_{AN} = 0.3$ and $\tau_0 = 7.0 \times 10^{-12}$ sec. and the broken lines are for mechanism (ii) with $K = 4.0$, $J_{BN}/J_{AN} = 0.3$, $2f(B)\tau_0 = 0.19$ rad./sec., $f(A)/f(B) = 0.5$ and $C_{AB} = 1.0$. For irradiation of line 3 $\blacktriangle A$ represents, in the definition of R , the ratio of line 4 to line 1 and $\bullet B$ the ratio of line 2 to line 1. For irradiation of line 4 $\circ C$ represents the ratio of line 2 to line 1 and $\triangle D$ the ratio of line 3 to line 1. For each place of irradiation three strengths 0.043, 0.076 and 0.135 Hz were used.



(for $J_{AN} \approx 9.7$ Hz and $J_{BN} \approx 2.9$ Hz) show large deviations from experimental values. These considerations show that the external random fields along with scalar coupling do not account for the observed changes in the spectra with 'low' amplitudes of irradiation and hence mechanism (ii) is ruled out. The internal dipole-dipole interaction along with the scalar coupling accounts for all the features of the single and double resonance spectra and is, therefore, the dominant mechanism for relaxation in this molecule. As the relaxation contribution of internal dipole-dipole interaction is strongly dependent on the distance between the interacting spins (r^{-6}), this result is not surprising in view of the small proton-proton distance (1.66 \AA), in this molecule, (compared to 2.48 \AA between the ortho protons in benzene). The viscosity of 2-bromothiazole was measured at room temperature and a value ≈ 2.0 centipoise obtained. This leads to a hard sphere radius (see Eq. V-1) of the order of 2 \AA , which fits well with the molecular dimensions in this case.

The theoretical spectra for mechanism (i) having $K = 4.0$ and $J_{BN}/J_{AN} = 0.3$ are plotted in juxtaposition with the double resonance spectra in Figs. (VI-5 and 6). These show good agreement between the observed and calculated spectra.

Table (VI-3) gives the contribution of internal dipole-dipole interaction and scalar coupling to the single resonance relaxation matrix elements of the type $R_{\alpha\alpha\beta\beta}$ and

Table VI-3

Contributions of internal dipole-dipole interaction and scalar coupling to various single resonance relaxation matrix elements (in rad./sec.) for mechanism (i) having $K = 4.0$, $J_{BN}/J_{AN} = 0.3$ and $\tau_c = 7.0 \times 10^{-12}$ sec.

Matrix element†	Dipole-dipole	Scalar coupling	Total
1 2 1 2	-0.174	-0.149	-0.323
1 3 1 3	-0.149	-1.508	-1.657
1 4 1 4	-0.171	-2.565	-2.737
2 3 2 3	-0.076	-0.731	-0.808
2 4 2 4	-0.174	-1.508	-1.681
3 4 3 4	-0.149	-0.149	-0.298
1 1 1 1	0.171	0.000	0.171
1 1 2 2	0.035	0.000	0.035
1 1 3 3	0.021	0.000	0.021
1 1 4 4	0.114	0.000	0.114
2 2 2 2	-0.086	-0.013	-0.099
2 2 3 3	0.018	0.013	0.031
2 2 4 4	0.034	0.000	0.034
3 3 3 3	-0.065	-0.013	-0.078
3 3 4 4	0.023	0.000	0.023
4 4 4 4	-0.171	0.000	-0.171

† The numbering of the states is such that for the AB spin system, in the zeroth order these states are given, in the increasing order by, $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$.

$R_{\alpha\beta\alpha\beta}$ for the parameters for which a satisfactory fit of the double resonance spectra has been obtained. This table shows the relative contribution of these two mechanisms to the relaxation in this spin system.

It is concluded from this study that the internal dipole-dipole interaction and the scalar coupling of the protons with nitrogen, which is relaxing rapidly due to quadrupole relaxation, in 2-bromothiazole, accounts for proton relaxation in this molecule and that the external random fields do not contribute significantly to the relaxation processes. Various parameters describing the internal dipole-dipole interaction ($\tau_c \approx 7.0 \times 10^{-12}$ sec.), and the scalar coupling mechanism ($J_{AN} \approx 9.7$ Hz, $J_{BN} \approx 2.9$ Hz and of the same sign) have also been obtained.

SUMMARY AND CONCLUSIONS

Relaxation processes in coupled spin systems have been studied by steady-state homonuclear double resonance experiments. The systematics of the double resonance method and details of the relaxation processes have been examined. Double resonance experiments have been performed on a coupled symmetrical three spin system (AB_2) and on an AB spin system.

It is found that it is useful to study double resonance spectra obtained over a wide range of strengths of irradiation, as the solution of the density-matrix equations obtained for conditions of 'high' and 'low' irradiation amplitudes possess some distinctive features which may then be used with considerable advantage to distinguish between different relaxation mechanisms. A detailed consideration of the inhomogeneity of the magnetic field is shown to be of crucial importance for the analysis of the relaxation effects and a method of including it in the density matrix calculations of the double resonance spectra is suggested. The inhomogeneity of the magnetic field is found to contribute a full-width at half-height of the order of 0.15 Hz to single resonance transitions, in the present experiments, which was almost wholly recoverable in double resonance spectra under suitable experimental conditions.

Isotropic random field model, convenient for description of relaxation effects in such studies, is shown to be

a plausible model for various intermolecular and intramolecular interactions under conditions normally realised in experiments. Whenever such a model is applicable the constants describing the correlation between the random fields at the sites of different spins have been discussed. A definition of this constant, which includes the possibility of completely correlated fields with different mean square values, is used.

The relaxation of the AB_2 spin system of the ring protons of 2,6-dibromoaniline, which was studied as a 20 per cent solution in CCl_4 , is found to be predominantly due to external random fields having mean square value twice at the site of 'A' proton compared to either of the two 'B' protons. The random fields at the two 'B' protons are found to be highly correlated, while those at 'A' and any of the 'B' protons being almost uncorrelated. Intermolecular dipolar interaction between the protons and the chlorine nuclei of the solvent appears to be the source for these random fields. The effect of intramolecular dipolar interactions between the various protons, within the spin system, is small compared to that due to the intermolecular random fields.

The relaxation of the AB spin system of the protons of 2-bromothiazole, studied as a neat liquid, is, on the other hand, found predominantly by the intramolecular dipolar interaction between the two protons and by their scalar coupling with the nearby N^{14} , which in turn is relaxing fast

due to quadrupolar relaxation. The intramolecular dipolar interaction is significant in this molecule because the proton-proton distance is small compared to ^{that} in molecules like benzene. External random fields do not seem to contribute significantly in this molecule. Double resonance experiments performed over a wide range of strengths of irradiation and at various frequencies of irradiation led to the determination of the magnitudes and relative sign of proton- N^{14} scalar coupling constants. The various parameters describing the proton relaxation are, $\tau_0 = 7.0 \times 10^{-12}$ sec., $J_{AN} \approx 9.7$ Hz and $J_{BN} \approx 2.9$ Hz (for $\tau_q = 0.61$ millisecc); J_{AN} and J_{BN} have the same sign.

It may be noted that the presence of bromine does not modulate proton relaxation in both the above cases. The random fields arising due to the scalar coupling of protons and bromine are negligible presumably due to a fast quadrupole relaxation of bromine nuclei which possess a large quadrupole moment.

Further studies of this kind can be aimed at (i) studying the relative importance of dipole-dipole interaction and external random fields as a function of distance between the interacting spins, (ii) studies by double resonance in which scalar coupling is only partly "washed-out", (iii) relaxation effects in double resonance as a function of external parameters like temperature, external magnetic field etc., for determining the relative importance of various

interactions, in particular, that of the intramolecular and intermolecular dipole-dipole interactions, spin-rotation interaction, anisotropic chemical shift (if any). Further insight into the relaxation processes can also be gained by attempting to interpret the different values of the mean square random fields and their mutual correlations in terms of specific models for the dynamical behaviour of the liquid.

REFERENCES

- [1] Bloch, F., 1946, Phys. Rev., 70, 460.
- [2] Pople, J.A., Schneider, W.G., and Bernstein, H.J., 1959, "High Resolution Nuclear Magnetic Resonance", Chap. VI (New York: McGraw-Hill Book Company, Inc.).
- [3] Wangsness, R.K., and Bloch, F., 1953, Phys. Rev., 89, 728.
- [4] Bloch, F., 1956, Phys. Rev., 102, 104.
- [5] Baldeschwieler, J.D., 1964, J. Chem. Phys., 40, 459; [5a] 1961, *ibid.*, 34, 718.
- [6] Redfield, A.G., 1957, IBM J. Res. Dev., 1, 19; 1965, "Advances in Magnetic Resonance", Vol. 1, edited by J.S. Waugh (London, New York: Academic Press), p. 1.
- [7] Abragam, A., 1961, "Principles of Nuclear Magnetism", Chap. VIII, (Oxford University Press).
- [8] Hubbard, P.S., 1961, Rev. Mod. Phys., 33, 249.
- [9] Nageswara Rao, B.D., 1965, Phys. Rev., A137, 467.
- [10] Anup Kitchlew, Anil Kumar and Nageswara Rao, B.D., 1968, Chem. Phys. Lett., 2, 216.
- [11] Nageswara Rao, B.D., Baldeschwieler, J.D., and Anderson, J.M., 1965, Phys. Rev., A137, 1477.
- [12] Wakefield, R.H., and Memory, J.D., 1968, J. Chem. Phys., 48, 2174.
- [13] Matsuoka, M., and Kakiuchi, Y., 1965, J. Phys. Soc. Japan, 20, 1174.
- [14] Noggle, J.H., 1965, J. Chem. Phys., 43, 3304; 1964, "thesis", Harvard University, Cambridge, Massachusetts, U.S.A., (unpublished).
- [15] Kuhlmann, K.F., and Baldeschwieler, J.D., 1965, J. Chem. Phys., 43, 572.
- [16] Nageswara Rao, B.D., and Lessinger, L., 1967, Molec. Phys., 12, 221.

- [17] Freeman, R., Ernst, R.R., and Anderson, W.A., 1967, *J. Chem. Phys.*, 46, 1125.
- [18] Nageswara Rao, B.D., and Anders, L.R., 1965, *Phys. Rev.*, A140, 112.
- [19] Gordon, S.L., and Baldeschwieler, J.D., 1964, *J. Chem. Phys.*, 41, 571.
- [20] Gordon, S.L., and Baldeschwieler, J.D., 1965, *J. Chem. Phys.*, 43, 76.
- [21] Gordon, S.L., 1968, *J. Chem. Phys.*, 48, 2129.
- [22] Kaiser, R., 1965, *J. Chem. Phys.*, 42, 1838.
- [23] Freeman, R., and Anderson, W.A., 1962, *J. Chem. Phys.*, 37, 2053.
- [24] Barfield, M., and Baldeschwieler, J.D., 1964, *J. Chem. Phys.*, 41, 2633.
- [25] Anderson, W.A., and Freeman, R., 1962, *J. Chem. Phys.*, 37, 85.
- [26] Nageswara Rao, B.D., "Advances in Magnetic Resonance", Vol. 4, edited by J.S. Waugh (London, New York; Academic Press), to be published.
- [27] Freeman, R., and Gestblom, B., 1967, *J. Chem. Phys.*, 47, 2744.
- [28] Baldeschwieler, J.D., and Randall, E.W., 1963, *Chem. Rev.*, 63, 81.
- [29] Bloembergen, N., Purcell, E.M., and Pound, R.V., 1948, *Phys. Rev.*, 73, 679.
- [30] Hubbard, P.S., 1962, *Phys. Rev.*, 128, 650.
- [31] Hubbard, P.S., 1963, *Phys. Rev.*, 131, 1155.
- [32] Huntress, W.T., 1968, *J. Chem. Phys.*, 48, 3524.
- [33] Krynicki, K., and Powles, J.G., 1965, *Proc. Phys. Soc. (London)*, 86, 549.
- [34] Brown, R.J.C., Gutowsky, H.S., and Shimomura, K., 1963, *J. Chem. Phys.*, 38, 76.

- [35] Hubbard, P.S., 1963, Phys. Rev., 131, 275.
- [36] Andrew, E.R., 1958, "Nuclear Magnetic Resonance", (Cambridge University Press),
- [37] Kintzinger, J.P., and Lehn, J.M., 1968, Molec. Phys., 14, 133.
- [38] Rama Krishna, M., Anil Kumar, and Nageswara Rao, B.D., unpublished calculations.
- [39] Pople, J.A., 1958, Molec. Phys., 1, 168.
- [40] Sack, R.A., 1958, Molec. Phys., 1, 163.
- [41] Anderson, P.W., 1954, J. Phys. Soc. Japan, 9, 316.
- [42] Nageswara Rao, B.D., and Baldeschwieler, J.D., 1962, J. Chem. Phys., 37, 2473.
- [43] Freeman, R., 1962, Molec. Phys., 5, 499.
- [44] Clarke, G.M., and Williams, D.H., 1965, J. Chem. Soc., 4597.
- [45] Anderson, W.A., 1960, "NMR and EPR Spectroscopy", (New York, Oxford, London, Paris; Pergamon Press), by NMR-EPR staff of Varian Associates, p. 169.
- [46] Smith, G.W., 1964, J. Applied Phys., 35, 1217.
- [47] Mme Emile-Jean Vincent and Jacques Metzger, 1965, C.R. Acad. Sci. (Fr.), 261, 1964.

APPENDIX I

LISTING OF COMPUTER PROGRAM

INTRODUCTION

The listing of a typical computer program used in the density-matrix analysis of the double resonance spectra, is given in the following. The program is written in Fortran IV and run on IBM 7044. This program in its present form is applicable upto three spin systems, but can easily be extended to larger spin systems. Further, this program calculates double resonance spectra for 'high' values of v_2 , for which Bloch approximation holds. For 'low' strengths of irradiation, the laboratory coordinate calculations have been performed by incorporating minor modifications to include the off-diagonal matrix element of χ .

In the first part of this program the spin hamiltonian matrix \mathcal{H}_0 is formed in the spin product basis. A matrix diagonalization routine is used to obtain the eigenvalues.[†] This routine also gives the transformation coefficients which are then used to transform various quantities from spin product basis to $\alpha, \alpha' \dots$ basis, in which \mathcal{H}_0^R is diagonal.

In the second part of the program, various relaxation matrix elements (R) are calculated by using a subroutine named RFDCAL. The relaxation matrix elements can be calculated for any degree of correlation. The simultaneous equations for matrix elements of $\tilde{\chi}$ are then formed and solved by using a determinant evaluation subroutine named DETER. In the last part the relative intensities of the double resonance transitions including relaxation effects are calculated.

+ This routine and a part of the remaining program are similar to those used by the magnetic resonance group at the Department of Chemistry, Harvard University, Cambridge, Mass., U.S.A. during 1961-65.

SUCC PHG007, TIME008, PAGES030, NAME ANIL

STBJOB

LIBFTC MAIN ODECK

C THIS PROGRAM CALCULATES DOUBLE RESONANCE SPECTRA USING EXTREME
C NARROWING ASSUMPTION AND BLOCH APPROXIMATION.
C NOSPIN IS THE ORDER OF THE SPIN SYSTEM CONSIDERED. NASSYM IS THE
C NUMBER OF ASYMMETRIC STATES. CHART IS THE SPEED OF CHART PAPER
C PER C.P.S. AND GIVES DIRECT CALIBRATION OF THE SPECTRA.
C THE F ARE COMPONENTS OF LATTICE FUNCTIONS IN THE IRREDUCIBLE FORM
C THESE MAY BE EXPRESSED WITHIN A PROPORTIONALITY CONSTANT
C NOFX IS THE NUMBER OF COMPONENTS OF LATTICE OPERATORS.
C AS STORES THE MATRIX ELEMENTS OF THE RELAXATION HAMILTONIAN IN THE
C SPIN PRODUCT BASIS, FED AS INPUT DATA. THE CHEMICAL SHIFT (A-B),
C THE COUPLING CONSTANT J, THE AMPLITUDE OF IRRADIATION VA=VB AND THE
C FREQUENCY OF IRRADIATION (A=FREQ. OF A RESONANCE- FREQ. OF IRRAD.
C AND B=FREQ. OF B RESONANCE - FREQ. OF IRRAD.) ARE INPUT PARAMETERS
C C1, C2, AND C3 ARE THE DEGREE OF CORRELATION AND ARE TO BE FED AS
C INPUT PARAMETERS.

C PROGRAM FOR BLOCH APPROXIMATION

C NMDR THREE SPIN 1/2

```

      DIMENSION ABC(8,8,15),F(15),AS(8,8,15),ROOT(10),AA(10,10)
      DIMENSION X(8,8),Y(8,8),E(8,8),H(8)
      DIMENSION U(10,10),V(8),SIGMA(10,10),REPVEC(10)
      DIMENSION RAAB(10,10),RADAB(8,8),RAABC(8,8,8)
      COMMON NOSPIN,NQMAX,F
      COMMON /ANIL/ABC,C1,C2,C3
      COMMON /KUMAR/NSYM
      STWO=SQRT(2.0)
      READ1007,CHART
      PRINT1010,CHART
      4 READ1009,NOSPIN,NASSYM
      NDIM=2*NOSPIN
      ISYM=NDIM-NASSYM
      PRINT1006
      7 READ1005
      PRINT1003
      READ1009,NQMAX
      DO121NQ=1,NQMAX
      DO 120 I=1,NDIM
      DO 120 J=1,NDIM
120  AS(I,J,NQ)=0.0
      DO141NQ=1,NQMAX
110  READ1030,I,J,ASS
      IF(I.EQ.0)GO TO 121
      AS(I,J,NQ)=ASS
      PRINT1031,I,J,NQ,ASS
      GO TO119
121  CONTINUE
      8 READ1007,(F(I),I=1,NQMAX)
      PRINT1007,(F(I),I=1,NQMAX)

```

C
C X(I,J) ARE THE MATRIX ELEMENTS OF THE SPIN HAMILTONIAN IN THE SPIN
C PRODUCT BASIS
C FOR DIFFERENT SPIN SYSTEMS THE FOLLOWING CARDS HAVE TO BE CHANGED
C THE PRESENT SET OF CARDS ARE FOR AN AB2 TYPE OF SPIN SYSTEM.
C THE ANTISYMMETRIC STATES, IF ANY, SHOULD BE THE LAST PAIR OF STATES.

```

1 READ 1007,A,B,R,VA,VB
PRINT1006
PRINT1007,A,B,R,VA,VB
C COMPUTE X MATRIX
4 DO 5 I=1,NDIM
DO5 J=1,NDIM
5 X(I,J)=0.
X(1,1)=(A+2.*B+R)/2.
X(2,2)=(-A+2.*B-R)/2.
X(3,3)=A/2.
X(4,4)=-A/2.
X(5,5)=(A-2.*B-R)/2.
X(6,6)=(-A-2.*B+R)/2.
X(7,7)=A/2.
X(8,8)=-A/2.
X(1,3)=VB/STWO
X(1,2)=VA/2.
X(2,4)=VB/STWO
X(3,5)=VB/STWO
X(4,6)=VB/STWO
X(3,4)=VA/2.
X(4,5)=R/STWO
X(2,3)=R/STWO
X(5,6)=VA/2.
X(7,8)=VA/2.
DO 3 I=1,NDIM
DO 3 J=I,NDIM
3 X(J,I)=X(I,J)
C
C MATRIX DIAGONALIZATION ROUTINE
C ARRAYS USED X(I,J), E(I,J)(EIGNEVECTORS), DIMENSION-NDIM
C FIND LARGEST OFF DIAGONAL X
C
250 DO 253 I=1,NDIM
DO 253 J=1,NDIM
IF(I-J) 251,252,251
251 E(I,J)=0.
GO TO 253
252 E(I,J)=1.0
253 CONTINUE
200 LA=1
LP=2
BX=ABS(X(2,1))
DO 202 J=3,NDIM
JA=J-1
DO 202 I=1,JA
D=BX-ABS(X(I,J))
IF(D) 201,202,202
201 BX=ABS(X(I,J))
LA=I
LB=J
202 CONTINUE
IF(BX-0.00001) 320,320,300
C COMPUTE ROTATION

```

```

300 BX=X(LA, LB)*X(LA, LB)
    D=X(LA, LA)-X(LB, LB)
    R=SQRT(D*D+4.*BX)
    A=SQRT(ABS((R+D)/(2.*R)))
    IF(0.707-A) 302,302,301
301 B=0.0-A
    A=SQRT(1.0-B*B)
    GO TO 303
302 E=-SQRT(1.0-A*A)
303 IF(D/X(LA, LB)) 304,310,310
304 B=0.0-B
C   ORTHOGONAL ROTATION OF MATRIX
310 DO 313 J=1,NDIM
    IF(LA-J) 311,313,311
311 IF(LB-J) 312,313,312
312 X(LA, J)=A*X(J, LA)-B*X(J, LB)
    X(LB, J)=B*X(J, LA)+A*X(J, LB)
313 CONTINUE
    DO 314 J=1,NDIM
    X(J, LA)=X(LA, J)
314 X(J, LB)=X(LB, J)
    D=X(LA, LA)+X(LB, LB)
    X(LA, LA)=A*A*X(LA, LA)+B*B*X(LB, LB)-2.*A*B*X(LA, LB)
    X(LB, LB)=D-X(LA, LA)
    X(LA, LB)=0.0
    X(LB, LA)=0.0
C   ENTER ROTATION IN E MATRIX
    DO 315 J=1,NDIM
    BX=E(J, LA)
    E(J, LA)=A*BX-B*E(J, LB)
315 E(J, LB)=B*BX+A*E(J, LB)
    GO TO 200
C   TEST DIAGONALIZED MATRIX
320 BX=1.00E-04
    JA=NDIM-1
    DO 323 I=1, JA
    JB=I+1
    DO 323 J=JB,NDIM
    IF(X(I, J)) 321,323,321
321 R=ABS(X(I, J)/(X(I, I)-X(J, J)))
    IF(R-BX) 323,323,322
322 BX=R
    LA=I
    LB=J
323 CONTINUE
    IF(BX-0.00005) 450,450,300
C   CALC TRANSITION INTENSITIES AND FREQUENCIES
450 DO 451 I=1,NDIM
    H(I)=X(I, I)
    DO 451 J=1,NDIM
451 X(I, J)=0.0
C
C   THE FOLLOWING ARE MATRIX ELEMENTS OF I(+) IN SPIN PRODUCT BASIS.
C   THESE CARDS HAVE TO BE CHANGED FOR DIFFERENT SPIN SYSTEMS.

```

```

C
  V(1,2)=1.0
  X(1,3)=STWO
  X(2,4)=STWO
  X(3,5)=STWO
  X(4,6)=STWO
  X(5,6)=1.0
  X(7,8)=1.0
452 DO 453 I=1,NDIM
    DO 453 J=1,NDIM
      Y(I,J)=0.0
      DO 453 LA=1,NDIM
        DO 453 LB=1,NDIM
453   Y(I,J)=Y(I,J)+ E(LA,I)*X(LA,LB)*E(LB,J)
        PRINT 1001
        DO 456 I=1,NDIM
          PRINT 1002,I,H(I)
          DO 456 J=1,NDIM
            R=H(I)-H(J)
            YSQ=V(I,J)*Y(I,J)
            PLOT=R*CHART
456   PRINT 1003,J,R,YSQ,Y(I,J),E(I,J),PLOT
C   CALCULATION OF REDFIELD ELEMENTS
C   TRANSFORM RELAXATION MATRIX
    DO130 NQ=1,NQMAX
    DO 130 I=1,NDIM
    DO 130 J=1,NDIM
      ABC(I,J,NQ)=0.0
      DO130 K=1,NDIM
      DO 130 L=1,NDIM
130   ABC(I,J,NQ)=ABC(I,J,NQ)+E(K,I)*AS(K,L,NQ)*F(L,J)
C   FORM SIGMA MATRIX AND TRANSFORM IT
    DO515 I=1,NDIM
    DO515 J=1,NDIM
515   X(I,J)=0.0
C
C   THE FOLLOWING GIVE -F(Z)=-SUM(I(I(Z))) IN THE SPIN PRODUCT BASIS.
C   THESE ARE THUS MATRIX ELEMENTS OF SIGMA ZERO IN SPIN PRODUCT BASIS.
C   THESE CARDS HAVE TO BE CHANGED FOR DIFFERENT SPIN SYSTEMS.
C
  X(1,1)=-1.5
  X(2,2)=-0.5
  X(3,3)=-0.5
  X(4,4)= 0.5
  X(5,5)= 0.5
  X(6,6)= 1.5
  X(7,7)=-0.5
  X(8,8)= 0.5
C   TRANSFORM SIGMA MATRIX
  PRINT 1020
  DO517 I=1,NDIM

```

```

      DO516J=1,NDIM
      SIGMA(I,J)=0.0
      DO516L=1,NDIM
      DO516K=1,NDIM
515 SIGMA(I,J)=SIGMA(I,J)+E(K,I)*X(K,L)*E(L,J)
517 PRINT1003,(SIGMA(I,J),J=1,NDIM)
      PRINT1006
C     READ CORRELATION
      C READ 1002,NCCRLN
      DO900 IJK=1,NCORLN
C   C1, C2 AND C3 ARE CORRELATIONS.
      9 READ1007,C1,C2,C3
458 PRINT 1006
      PRINT1024,C1,C2,C3
      PRINT1006
C   CALCULATION OF R(IIJJ)
      DO510I=1,NSYM
      DO509J=1,NSYM
      CALL RFDICAL(I,I,J,J,RFD)
      RAABB(J,I)=RFD
509 RAABE(I,J)=RFD
510 CONTINUE
      DO512J=1,NSYM
      DO512K=J,NSYM
      IF(J.EQ.K) GO TO 512
      DO511I=1,NSYM
      CALL RFDICAL(I,I,J,K,RFD)
      RAABC(I,J,K)=RFD
511 RAAC(I,K,J)=RFD
512 CONTINUE
      DO514I=1,NDIM
      DO510J=1,NDIM
      IF(I.EQ.J) GO TO 513
      CALL RFDICAL(I,J,I,J,RFD)
      RAAB(I,J)=RFD
      RAAB(J,I)=RFD
513 CONTINUE
      II=I+1
514 PRINT1015,((RAAB(I,J),I,J,I,J),J=II,NDIM)
C   SOLUTION OF SIMULTANEOUS EQUATIONS
      DO520I=1,NSYM
      V(I)=0.
      DO520J=1,NSYM
      DO520K=J,NSYM
      IF(J.EQ.K) GO TO 520
      V(I)=V(I)+2.0*SIGMA(J,K)*RAABC(I,J,K)
520 CONTINUE
      PRINT1018
      DO524I=1,NSYM
524 PRINT1019,(RAAB(I,J),J=1,NSYM),V(I)
      PRINT1006
      CALL DETER(RAAB,DET)

```

```

      PRINT1011,DET
C   CHECK FOR LINEAR DEPENDENCE
      DO530K=1,NSYM
      DO545I=1,NSYM
      DO525J=1,NSYM
      REPVFC(I)=V(I)
523  U(I,J)=RAAB2(I,J)
      DO546J=1,NSYM
526  U(K,J)=1.0
      REPVFC(K)=0.0
      CALL DETER(J,DET)
      PRINT1021,K,DET
      CHECK=ABS(DET)
      IF(CHECK-0.0001) 530,540,541
530  CONTINUE
540  IF(CHECK.LT.0.0001) GO TO 900
      DO550K=1,NSYM
      DO571J=1,NSYM
      DO571I=1,NSYM
      AA(I,J)=U(I,J)
      IF(J-K) 571,570,571
570  AA(I,K)=REPVFC(I)
571  CONTINUE
      CALL DETER(AA,DEM)
      ROOT(K)=DEM/DET
      PRINT1006
580  PRINT1012,K,DEM,K,ROOT(K)
C   CHECK THE ROOTS
      PRINT1006
      PRINT1016
      DO584K=1,NSYM
      EQ=0.0
      DO593J=1,NSYM
583  EQ=EQ+ROOT(J)*U(K,J)
584  PRINT1017,K,EQ,REPVFC(K)
C   CALCULATION OF SIGNAL INTENCITIES
      PRINT1006
      PRINT1026
      DO610I=1,NDIM
      PRINT1002,I,H(I)
      DO610J=1,NDIM
      IF(I.EQ.J) GO TO 610
      SIG=Y(I,J)*Y(I,J)*(SIGMA(J,J)-SIGMA(I,I)+ROOT(J)-ROOT(I))
      SIGINT=SIG/RABAB(I,J)
      FREQ=H(I)-H(J)
      PLOT=FREQ*CHART
      PRINT1003,J,FREQ,SIG,SIGINT,PLOT
610  CONTINUE
900  CONTINUE
      PRINT1006
      PRINT1006
      GO TO 1

```

```

1001 FORMAT(/3H A=,F10.5,4H 0=,F10.5,4H R=,F10.5,5H VA=,F7.3,5H VB=
1,F7.3//)
1002 FORMAT(2H 1,6X,4HE(I),8X,2H J,8X,4HFREQ,9X,3HINT,8X,10HTRANS (I+)
1,4X,11HTRANS COEFF,*, CHART*/)
1003 FORMAT(I2,F12.5)
1004 FORMAT(2CX,I2,5F14.5)
1005 FORMAT(2F18.8)
1006 FORMAT(*)
1007 FORMAT(/)
1008 FORMAT(8F10.5)
1009 FORMAT(10F12.5)
1010 FORMAT(5I5)
1011 FORMAT(* NO OF CMS. PER C.P.S. =*,F10.5/)
1012 FORMAT(* DET=*,E12.5/)
1013 FORMAT(5H DEM(,I1,4H) = ,E12.5,10H ROOT(,I1,4H) = ,E12.5)
1014 FORMAT(4(F18.8,* = R(*,4I1,*))* )
1015 FORMAT(29H CALCULATED VALUE OF EQUATION,5X,15H SUPPLIED VALUE)
1016 FORMAT(5X,1H(,I2,3H) =,F10.6,15X,F10.6)
1017 FORMAT(40X,*A(I,J)*,50X,*V(I)*//)
1018 FORMAT(8F12.5,6X,F12.5)
1019 FORMAT(/35X,*SIGMA ZERO MATRIX*/)
1020 FORMAT(* EQUATION REPLACED=*,I2,* DET=*,E12.5/)
1021 FORMAT(10X,* MATRIX ELEMENTS OF I(+)* )
1022 FORMAT(2I5,*=*,F10.5)
1023 FORMAT(* C1=*,F10.5,* C2=*,F10.5,* C3=*,F10.5)
1024 FORMAT(* I=,6X,*E(I)*,8X,* J=,8X,*FREQ*,11X,*INT*,6X,*INT/RIJIJ*,
18X,*CHART*/)
1025 FORMAT(2I5,F13.8)
1026 FORMAT(* AS(*,I1,*=*,I1,*=*,I2,*)=*,F13.8)
END
SIBFTC SUB1 NODECK
SUBROUTINE RFDCL(I,J,K,L,RFD)
C THIS SUBROUTINE CALCULATES THE RELAXATION MATRIX ELEMENTS R.
C PARTIAL CORRELATION WITH EITHER EXTREMES OF COMPLETE OR NO CORRELATION
C IS POSSIBLE. THE INPUT IS FROM MAIN PROGRAM AND THE RESULT IS
C STORED IN RFD.
DIMENSION A(8,8,15),F(15)
COMMON NOSPIN,NQMAX,F
COMMON/ANIL/ A , C1,C2,C3
N=I-2**NOSPIN
NOOP=NQMAX/NOSPIN
RFD=0.0
DO 230 NQ=1,NQMAX
IQ=NQ+NOOP
JQ=NQ+NOOP
LQ=NQ-NOOP
JQ=LQ-NOOP
RQ=0.0
RQ=RQ+A(I,K,NQ)*A(J,L,NQ)*F(NQ)
IF(NQ.LE.NOOP)RQ=RQ+C1*SQRT(F(NQ)*F(MQ))*A(I,K,NQ)*A(J,L,IQ)+
1C2*SQRT(F(NQ)*F(IQ))*A(I,K,NQ)*A(J,L,IQ)
IF(NQ.GT.NOOP.AND.LQ.LE.NOOP)RQ=RQ+C3*SQRT(F(NQ)*F(MQ))*A(I,K,NQ)*

```



```

14(J,L,Q)+C1*SQRT(F(LQ)*F(NQ))*A(I,K,NQ)*A(J,L,LQ)
  IF(JL.GT.NOOP)RQ=RQ+C2*A(I,K,Q)*A(J,L,JQ)*SQRT(F(NQ)*F(JQ))+C3*
15SQRT(F(NQ)*F(LQ))*A(I,K,NQ)*A(J,L,LQ)
  IF(J-L)220,210,220
210 IF(NQ-NOOP)212,212,211
211 IF(LQ-NOOP) 214,214,216
212 DO213 M=1,NDIM
  RQ=RQ-A(I,K,M)*A(M,I,Q)*F(NQ)/2.0
213 RQ=RQ-C1*A(I,K,Q)*A(M,I,NQ)*SQRT(F(NQ)*F(NQ))/2.0-C2*SQRT(F(NQ)*
  IF(IQ))*A(M,K,NQ)*A(M,I,IQ)/2.0
  GO TO 220
214 DO215M=1,NDIM
  RQ=RQ-A(I,K,NQ)*A(M,I,Q)*F(LQ)/2.0
215 RQ=RQ-C3*A(M,K,NQ)*A(M,I,Q)*SQRT(F(NQ)*F(IQ))/2.0-C1*SQRT(F(NQ)*
  IF(LQ))*A(M,K,NQ)*A(M,I,LQ)/2.0
  GO TO 220
216 DO217M=1,NDIM
  RQ=RQ-A(M,K,NQ)*A(M,I,NQ)*F(NQ)/2.0
217 RQ=RQ-C2*A(M,K,NQ)*A(M,I,JQ)*SQRT(F(NQ)*F(JQ))/2.0-C3*SQRT(F(NQ)*
  IF(LQ))*A(M,K,NQ)*A(M,I,LQ)/2.0
220 IF(I-K)230,221,230
221 IF(NQ-NOOP)223,223,222
222 IF(LQ-NOOP)225,225,227
223 DO224 M=1,NDIM
  RQ=RQ-A(M,I,NQ)*A(M,J,NQ)*F(NQ)/2.0
224 RQ=RQ-C1*A(I,L,NQ)*A(M,J,IQ)*SQRT(F(NQ)*F(IQ))/2.0-C2*SQRT(F(NQ)*
  IF(IQ))*A(I,L,NQ)*A(M,J,IQ)/2.0
  GO TO 230
225 DO226M=1,NDIM
  RQ=RQ-A(M,L,NQ)*A(M,J,NQ)*F(IQ)/2.0
226 RQ=RQ-C3*A(I,L,NQ)*A(M,J,IQ)*SQRT(F(NQ)*F(IQ))/2.0-C1*SQRT(F(NQ)*
  IF(LQ))*A(M,L,NQ)*A(M,J,LQ)/2.0
  GO TO 230
227 DO228M=1,NDIM
  RQ=RQ-A(M,L,NQ)*A(M,J,NQ)*F(NQ)/2.0
228 RQ=RQ-C2*A(M,L,NQ)*A(M,J,JQ)*SQRT(F(NQ)*F(JQ))/2.0-C3*SQRT(F(NQ)*
  IF(LQ))*A(M,L,NQ)*A(M,J,LQ)/2.0
230 RFD=RFD+RQ
  RETURN
END
SIBFTC SUB2      NODECK
  SUBROUTINE DETER(B,DET)
C  THIS SUBROUTINE CALCULATES THE VALUES OF A DETERMINANT BY PIVOTAL
C  METHOD. NO IS THE ORDER OF THE DETERMINANT TO BE CALCULATED AND
C  DET IS ITS CALCULATED VALUE.
  COMMON/KUIAR/NO
  DIMENSION B(10,10),A(10,10),PROW(10)
  NUM=NO
  DFT=1.
  DO3I=1,NO

```

```

      DO3J=1,NO
3  A(I,J)=B(I,J)
4  DO6 I=1,NUM
      IF(A(1,M)-0.)9,6,9
6  CONTINUE
      DET=0.
      GO TO 18
9  PIVOT=A(1,M)
      DO7 I=1,NUM
        PROW(I)=A(I,M)
7  A(1,I)=A(1,I)/PIVOT
      DO13 I=2,NUM
        DO13 J=1,NUM
15 A(I,J)=A(I,J)-PROW(I)*A(1,J)
      DO20I=2,NUM
        DO20J=1,NUM
          IF(J-M)11,20,10
10 A(I-1,J-1)=A(I,J)
      GO TO 20
11 A(I-1,J)=A(I,J)
20 CONTINUE
      NUM=NUM-1
      DET=PIVOT*DET*((-1.)**(M+1))
      IF(NUM-2)18,16,4
16 DET=(A(1,1)*A(2,2)-A(1,2)*A(2,1))*DET
18 RETURN
19 END
$ENTRY

```

APPENDIX II

N.M.R. Spectra of 1,3-Difluoro-4,6-dinitrobenzene
and Solvent Effects on Coupling Constants.

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N.M.R. SPECTRA OF 1,3-DIFLUORO-4,6-DINITROBENZENE AND SOLVENT EFFECTS ON COUPLING CONSTANTS

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(Received 13 February 1967)

1. INTRODUCTION

The high resolution nuclear magnetic resonance spectra and the solvent and concentration dependence of the spin-spin coupling constant of 1,3-difluoro 4,6-dinitrobenzene are reported here. This molecule is a four spin system of the type ABX_2 (in the notation of [1]) with nuclei labelled as shown in figure 1.

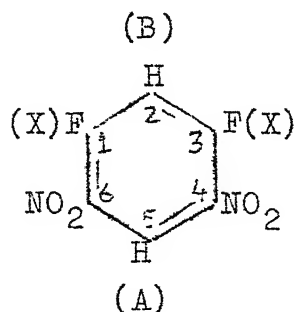
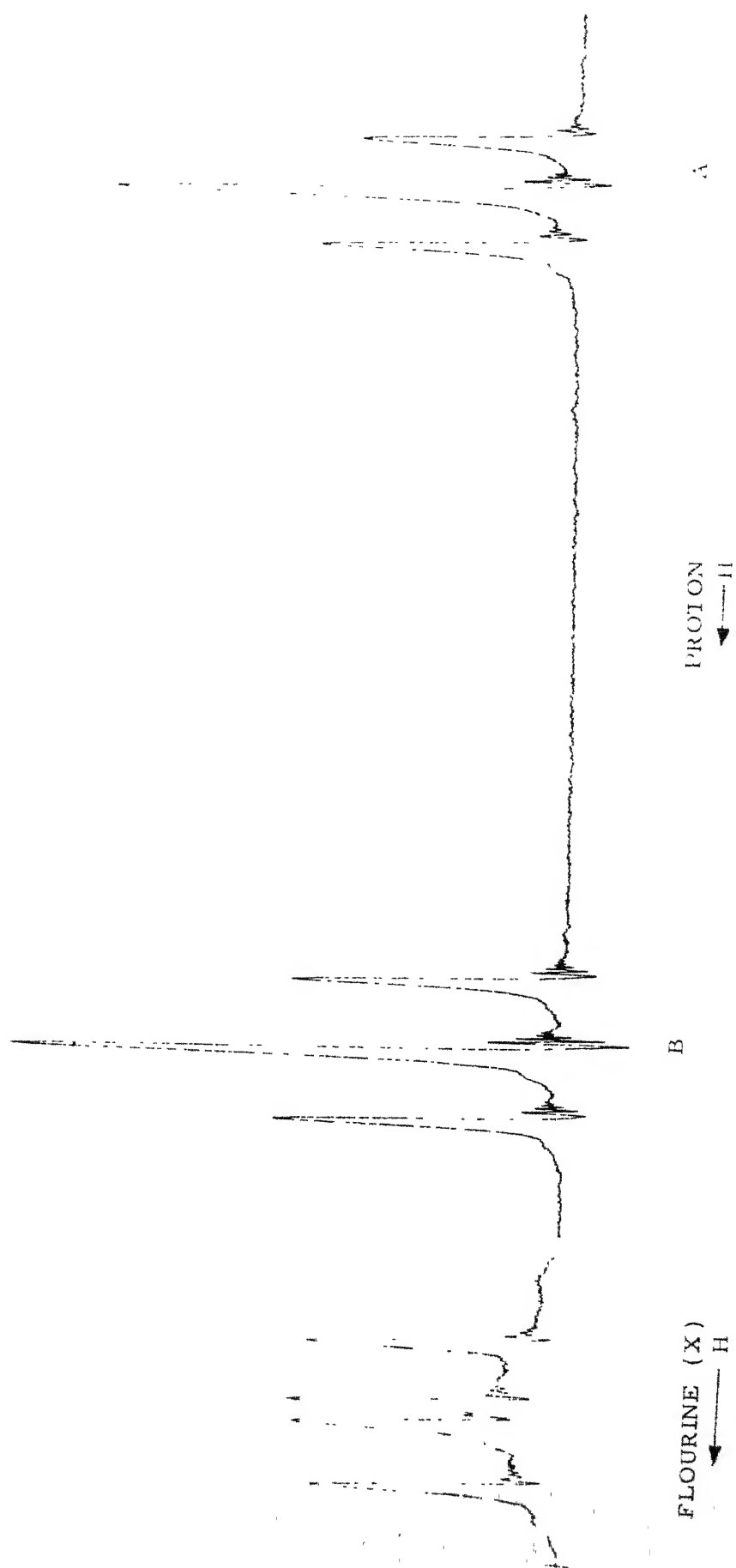


Figure 1. 1,3-difluoro-4,6-dinitrobenzene.

Analytical expressions can be derived for all the allowed transitions and their relative intensities [2]. The ^1H and ^{19}F resonance spectra of the molecule, recorded on a Varian HR-100 spectrometer operating at 100 Mc/s and 94.1 Mc/s respectively are shown in figure 2. The observed

Fig. AII-2. Fluorine, X and proton, A and B, spectra of 1,3-difluoro-4,6-dinitrobenzene. The lines in A resonance are broader compared to B resonance, probably due to a small coupling of the A proton with nitrogen, in the nearby NO_2 group, which is relaxing rapidly due to quadrupole interaction. The separation between the outer lines of the triplets in A and B resonances is $2J_{\text{HF}}^{\text{O}}$ and $2J_{\text{HF}}^{\text{m}}$ respectively. In X resonance the separation between the outer lines is $(|J_{\text{HF}}^{\text{m}}| + |J_{\text{HF}}^{\text{O}}|)$ and that between the inner lines is $(|J_{\text{HF}}^{\text{O}}| - |J_{\text{HF}}^{\text{m}}|)$.



spectra, however, do not show any further structure, indicating that the para H-H coupling is less than 0.3 c.p.s. (\sim half the linewidth). Thus if J_{HH}^p is assumed to be zero for this system the observed proton and fluorine spectra give in a straightforward manner the values of the meta and ortho H-F coupling constants.

2. SOLVENT EFFECTS

1,3-difluoro-4,6-dinitrobenzene is a solid at room temperature and can be studied in high resolution through the use of a solvent. The spectra were studied in various solvents to see the effect, if any, on the spin coupling constants due to the solvent. The results are given in the table. In two of the solvents deuterio-chloroform and dioxane the spectra were studied at several different concentrations. The variation of the coupling constants with concentration, in the range of concentrations studied, is smaller than the variation in different solvents. The coupling constants tend to increase with percentage concentration in d-chloroform. This trend is reversed in dioxane and further the values are smaller in d-chloroform than in dioxane. The coupling constants in the pure compound therefore are expected to lie between the values in these two solvents.

The solvent and concentration dependence of coupling constants, except where they are due to configurational modifications, indicate changes in intramolecular

Solvent	Percentage conc. by wt.	$J_{AX=J_{HF}}^m$ c.p.s. [†]	$J_{BX=J_{HF}}^o$ c.p.s. [†]	$J_{HF}^m + J_{HF}^o$ c.p.s.	ϵ δ at 28°C	ν_A	ν_B	$\nu_A - \nu_B$	ν_X ¶
Benzene	10	7.00±0.08	10.01±0.04	17.01	2.27	127.1	597.7	470.4	-
d-chloroform	25	7.61±0.05	9.91±0.04	17.52		890.9	741.6	149.2	2660.8
	20	7.58±0.05	9.88±0.04	17.46		892.1	740.5	151.2	2678.6
	10	7.49±0.05	9.69±0.07	17.18	4.67	894.4	736.4	157.5	2689.5
	5	7.54±0.04	9.71±0.13	17.25	(CHCl ₃)	895.3	735.4	159.7	2702.1
Dichloromethane	10	7.61±0.04	9.93±0.05	17.54	3.79	890.7	735.6	155.2	-
Acetone	10	7.66±0.05	10.61±0.05	18.27	20.41	908.7	796.1	113.0	-
Acetonitrile	10	7.70±0.04	10.53±0.05	18.23	36.22	890.4	758.6	132.8	-
Tetrahydrofuran	10	7.65±0.04	10.58±0.05	18.23	8.20	906.3	787.1	119.7	-
Dioxane	25	7.71±0.04	10.59±0.05	18.30		912.0	783.7	128.1	-
	20	7.72±0.05	10.59±0.05	18.31		910.2	783.7	128.1	2386.7
	10	7.73±0.05	10.61±0.05	18.31	2.20	908.8	778.3	130.1	2368.4
	5	7.71±0.07	10.62±0.08	18.33		909.8	779.4	130.4	2362.2

† Standard deviation for about ten or more readings.

Contd.

§ Dielectric constants from: 1961, Handbook of Chemistry and Physics (Ohio: Chemical Rubber Co.). That of THF from: Meloon, C. A., and Kiser, R.W., 1963, Instrumental Analysis (Columbus, Ohio: Charles E. Merrill Books Inc.), p. 301.

|| Proton chemical shifts down field in c.p.s. from tetramethylsilane. These were obtained by noting the shifts from solvent signals (in the case of CDCl_3 , CHCl_3 was present as an impurity) and then correlated to TMS. by known δ values of these peaks (Varian associates N.M.R. Catalogs 1965).

¶ The fluorine chemical shifts down field in c.p.s. from the centre of the two signals of difluoroacetic acid used as an external reference. For the blank spaces no measurements were made.

Coupling constants and chemical shifts of 1,3-difluoro-4,6-dinitrobenzene.

The probe temperature for all the readings was 28°C .

interactions. The various factors considered responsible for these changes in ^1H - ^1H , ^1H - ^{19}F and ^{19}F - ^{19}F coupling constants, reported by several workers [3-8], include, the reaction field effects of the medium, molecular association, complex formation and the shape of the solvent and solute molecules. The reaction field [9] is an electric field produced at the solute molecule due to a polarization of the medium by the polar solute. The effect of this is indicated by similar changes in chemical shifts and coupling constants with dielectric constant of the solvent [3-8].

The present observed variation (table) of the sum of the two coupling constants ($|J_{\text{HF}}^{\text{o}}| + |J_{\text{HF}}^{\text{m}}|$)[†] at 10 per cent concentration in the first four solvents is approximately linear with dielectric constant. This variation is therefore likely to be due to the reaction field effects of the medium [3-8]. In the other three solvents namely acetonitrile, tetrahydrofuran and dioxane, the coupling constants bear no such relation to the dielectric constants. These three later solvents are known to be high donor centres [10] and will probably form donor-acceptor complexes by

[†] This sum, which can also be obtained directly from the fluorine spectra, shows a larger variation between solvents than either J_{HF}^{o} or J_{HF}^{m} separately. The similar variations of J_{HF}^{o} and J_{HF}^{m} with solvents indicate that these two coupling constants are of the same sign [6].

hydrogen bonding between the ring protons of the solute molecule and the donor centres of the solvent molecules [4,7]. The complex formation may affect the coupling constants in a way which is different from the reaction field.

Both the reaction field and the complex formation are also known to affect the chemical shifts [8,11] and therefore it is reasonable to expect some correlation between the variation of the coupling constants and that of the chemical shifts. An approximate correlation is obtained in the present case. The two coupling constants tend to increase with increasing chemical shifts, ν_A and ν_B and decreasing values of $(\nu_A - \nu_B)$ in agreement with previous observations [3-6]. The chemical shifts in benzene are, however, very different from those in other solvents, probably because benzene is an aromatic compound.

These observations suggest that the effect of the solvent on the coupling constants should be taken into account, particularly in solid samples where solvents are unavoidable. The apparent concentration independence of coupling constants within experimental errors could, in several cases, be due to the limited range of concentrations which could be studied (limited by solubility, signal-to-noise ratio, etc.) rather than the absence of any solvent effects. Therefore, the solvent dependence of coupling constants should be determined by studying the concentration

dependence in at least two solvents of different natures, and the pure compound values obtained by extrapolation, just as is the practice for chemical shifts. Conclusions arrived at otherwise could be erroneous [12]. The study of solvent dependence of the coupling constants should also throw some light on the various intramolecular interactions responsible for the coupling between two spins in a molecule.

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REFERENCES

- [1] Pople, J.A., Schneider, W.G., and Bernstein, H.J., 1959, "High Resolution Nuclear Magnetic Resonance", Chap. 6 (New York: McGraw-Hill).
- [2] Mortimer, F.S., 1959, J. Mol. Spectrosc., 3, 335. Cohen, A.D., and Sheppard, N., 1959, Proc. R. Soc. A, 252, 488. de Kowalewski, D.G., and Kowalewski, V.J., 1961, J. Phys. Radium, Paris, 22, 129.
- [3] Watts, V.S., and Goldstein, J.H., 1963, J. Mol. Spectrosc., 11, 325; 1965, J. Chem. Phys., 42, 228. Shapiro, B.L., Ebersole, S.J., and Kopshik, R.M., 1963, J. Mol. Spectrosc., 11, 326; 1963, J. Chem. Phys., 39, 3154.

- [4] Bates, P., Cawley, S., and Danyluk, S.S., 1964, J. Chem. Phys., 40, 2415.
- [5] Hutton, H.M., and Schaefer, T., 1965, Can. J. Chem., 43, 3116. Ng, S., Tang, J., and Sederholm, C.H., 1964, J. Chem. Phys., 40, 2090; 1965, *ibid.*, 42, 79.
- [6] Smith, S.L., and Cox, R.H., 1965, J. Mol. Spectrosc., 16, 216; 1966, J. Chem. Phys., 45, 2848.
- [7] Frankiss, S.G., 1963, J. Phys. Chem., 67, 752.
- [8] Evans, D.F., 1963, J. Chem. Soc., p. 5575.
- [9] Buckingham, A.D., Schaefer, T., and Schneider, W.G., 1960, J. Chem. Phys., 32, 1227; 1960, Can. J. Chem., 38, 300.
- [10] Briegleb, G., 1961, "Elektronone-Donator-Acceptor-Komplexe" (Berlin, Göttingen, Heidelberg: Springer-Verlag).
- [11] Reference [1], Chap. 15.
- [12] Nageswara Rao, B.D., 1963, Molec. Phys., 7, 307. Schaefer, T., 1962, Can. J. Chem., 40, 431.